UNIVERSIDAD POLITÉCNICA DE MADRID
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**RELATIONSHIP BETWEEN
RESIDUAL STRESSES AND
MECHANICAL BEHAVIOR IN
CERAMIC COMPOSITES**

Ph.D. THESIS

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and Mechanical Behavior in Ceramic
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Ph.D. THESIS

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Abstract

In present work, Alumina/Y-TZP (tetragonal ZrO_2 stabilized with 3 mol% Y_2O_3) materials, as an popular ceramic system with improved mechanical properties compared with the pure alumina ceramics, have been studied in terms of mechanical properties and residual stresses.

The novel tape casting method, which involved the stacking of green ceramics tapes at room temperature and using low pressures, is selected for manufacturing and investigation, in order to take full advantage of the future development of alumina-zirconia laminated materials. Features of materials obtained by the new processing method are determined and compared with those of materials obtained by conventional slip casting in a plaster mold, in order to study whether the proposed method of processing affects microstructure and thereby the mechanical properties and residual stresses characteristics of materials. To analyse the adequacy of the manufacturing process used to avoid the presence of discontinuities at the interfaces between the sheets and other phenomena that interfere with the mechanical properties, ceramic materials with the same composition in tapes were investigated.

Moreover, the effect of addition of zirconia on residual stress development of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ ceramics were taken into investigations, considering its significantly influence on the microstructure and mechanical properties of materials as well as the requirement of co-sintering of layers with different composites in laminated materials.

The characterization includes density, microstructure, mechanical properties (elastic modulus, hardness, flexure strength and fracture toughness) and residual stresses. Except of the traditional measurement methods, nanoindentation technique was also used as an additional measurement of the elastic modulus and hardness.

Neutron diffraction, both the constant-wavelength (CW) and time-of-flight (TOF) neutron diffraction techniques, has been used for reliable through-thickness residual strain measurement in bulk samples. Residual stresses were precisely determined combined with appropriate analysis methods, e.g. the Rietveld refinement. The phase compositions in sintered ceramics especially the ones of zirconia were accurately examined by Rietveld analysis, considering the complex polymorph of ZrO_2 and the possible phase transformation during manufacturing process.

Effects of Y-TZP content and the new processing method on the microstructure, mechanical performance and residual stresses were finally summarized in present studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials. The toughening mechanisms, especially the residual stresses related toughening, were theoretically discussed.

Resumen

En este trabajo, materiales de tipo alúmina/Y-TZP (ZrO_2 tetragonal, estabilizada con 3 mol. % Y_2O_3), como sistema cerámico popular por sus mejoradas propiedades mecánicas en comparación con las cerámicas de alúmina puras, han sido estudiados en términos de propiedades mecánicas y tensiones residuales.

El novedoso método de colado en cinta, consistente en el apilamiento de cintas de cerámica verde a temperatura ambiente y el uso de bajas presiones, se ha escogido para la presente investigación con el fin de poder aprovechar al máximo el futuro desarrollo de materiales laminados de alúmina-óxido de circonio. Se han determinado las propiedades de los materiales obtenidos por este nuevo método de procesamiento comparándolas con las de los materiales obtenidos por “slip casting”, con el fin de analizar si el método propuesto afecta a la microestructura y, por tanto, a las propiedades mecánicas y tensiones residuales propias de estos materiales. Para analizar la idoneidad del proceso de fabricación, utilizado para evitar la presencia de discontinuidades en las intercaras entre las láminas así como otros fenómenos que puedan interferir con las propiedades mecánicas, se estudiaron materiales cerámicos con la misma composición en cintas.

Por otra parte también se analizó el efecto de la adición de óxido de circonio sobre la aparición de tensiones residuales en cerámicas $\text{Al}_2\text{O}_3/\text{Y-TZP}$, teniendo en cuenta su notable influencia sobre las propiedades microestructurales y mecánicas de los materiales, así como el requisito de co-sinterización de capas con diferentes materiales compuestos en materiales laminados.

La caracterización del material incluye la determinación de la densidad, el análisis de la microestructura, la obtención de las propiedades mecánicas (módulo de elasticidad, dureza, resistencia a la flexión y tenacidad de fractura) así como de las tensiones residuales. En combinación con otros métodos de medida tradicionales, la nanoindentación también se empleó como una técnica adicional para la medida del módulo de elasticidad y de la dureza.

Por otro lado, diferentes técnicas de difracción con neutrones, tanto las basadas en longitud de onda constante (CW) como en tiempo de vuelo (TOF), han sido empleadas para la medición fiable de la deformación residual a través del grosor en muestras a granel. Las tensiones residuales fueron determinadas con elevada precisión, aplicando además métodos de análisis apropiados, como por ejemplo el refinamiento de Rietveld. Las diferentes fases en cerámicas sinterizadas, especialmente las de zirconia, se examinaron con detalle mediante el análisis de Rietveld, teniendo en cuenta el complicado polimorfismo del Óxido de Zirconio (ZrO_2) así como las posibles transformaciones de fase durante el proceso de fabricación.

Los efectos del contenido de Y-TZP en combinación con el nuevo método de procesamiento sobre la microestructura, el rendimiento mecánico y las tensiones residuales de los materiales estudiados ($\text{Al}_2\text{O}_3/\text{Y-TZP}$) se resumen en el presente trabajo. Finalmente, los mecanismos de endurecimiento, especialmente los relacionados con las tensiones residuales, son igualmente discutidos.

CONTENTS

Acknowledgements	I
Abstract	III
Resumen	V
1. Introduction	1
1.1 Background.....	1
1.2 Objectives.....	2
1.3 Structure of the thesis	3
2. Literature Review	5
2.1 Residual Stresses.....	5
2.1.1 Definition and classification.....	6
2.1.2 Causes of residual stresses.....	8
2.1.3 Residual Stress Measurement Techniques.....	9
2.1.4 Theory basis of diffraction measurement	15
2.1.5 Stress determination by diffraction.....	17
2.1.6 Diffraction profile analysis	20
2.1.7 Software implementation.....	24

2.2	Al ₂ O ₃ /Y-TZP Ceramics System.....	25
2.2.2	Powder processing: Colloidal processing.....	29
2.2.3	Toughening mechanisms in the Al ₂ O ₃ /Y-TZP system.....	32
2.3	Present Investigation	35
3.	Experimental Work.....	37
3.1	Introduction.....	37
3.2	Materials Preparation.....	37
3.3	Characterization of Sintered Materials	39
3.3.1	Density	39
3.3.2	Microstructure Characterization	40
3.4	Mechanical Testing	42
3.4.1	Elastic modulus.....	42
3.4.2	Flexural strength	44
3.4.3	Hardness.....	44
3.4.4	Fracture toughness	45
3.4.5	Nanoindentation tests.....	50
3.5	Residual Stresses Measurement	52
3.5.1	Constant-wavelength neutron diffraction	53
3.5.2	Time-of-flight (TOF) neutron diffraction	57
3.5.3	Residual Stress determination	62
4.	Properties of Al₂O₃/Y-TZP composites.....	69
4.1	Density and Microstructure	70
4.2	Elastic Modulus.....	73
4.3	The Vickers Hardness.....	75
4.4	Flexure Strength	75

4.5 Fracture Toughness Assessment	79
4.5.1 The Single Edge Laser-Notch Beam method (SELNB).....	79
4.5.2 The indentation fracture (IF) method.....	87
4.5.3 Comparison between SELNB and IF.....	93
4.6 Nanoindentation Measurement.....	94
4.7 Summary and Conclusions	99
5. Residual Stresses Analysis of Al₂O₃/Y-TZP composites	103
5.1 Constant-wavelength Neutron Diffraction	104
5.1.1 Diffraction profiles analysis	104
5.1.2 Residual stress determination.....	111
5.2 TOF Neutron Diffraction.....	116
5.2.1 Neutron diffraction patterns and Rietveld analysis	117
5.2.2 Crystal structures.....	123
5.2.3 Stress determination.....	126
5.2.4 Diffraction line broadening.....	137
5.3 Contribution of Residual Stresses to Mechanical Properties	142
5.3.1 Residual stress & Crack deflection.....	143
5.3.2 Residual stress & transformation toughening & microcracking...	147
5.4 Summary and Conclusion.....	148
6. Conclusions and Future Work	151
6.1 Conclusions.....	151
6.2 Future Work	153
Bibliography.....	155
List of Figures	175
List of Tables	181

Chapter 1

Introduction

1.1 Background

Alumina-based ceramic composites are considered as a candidate material for certain structural applications, such as thermal insulation barriers in motors and turbines, cutting tools, high temperature filtering and biomedical application [1, 2], because of their excellent resistance to wear, high hardness, resistance to corrosion, chemical stability behavior, good mechanical properties at high temperatures and relatively cheap technology of production. The primary disadvantage of ceramic materials is their inherent brittle nature. Efforts have been made for decades to improve the mechanical properties of ceramics by employing various manufacturing techniques and toughening mechanisms.

In most cases, the improved performance has been attributed to the development of beneficial residual stresses (RS). Residual stresses usually arise in manufacturing process, such as during cooling from the sintering temperature, due to the differences in thermal expansion coefficients and elastic modulus of its matrix and reinforcement. As stresses that can remain in the structure without any external applied load, residual stresses are superimposed on the applied stress field, and can either reduce, or enhance, the service life and performance of the materials.

In order to improve the durability and the structural integrity of ceramic composites, as well as optimizing the design criteria in applications, it is necessary to determine and understand the nature and magnitude of residual stresses precisely. Nevertheless, definitive experimental support of the precise distribution of RS is sometimes lacking and limited by measurements, partly since RS determination is usually done by laboratory-based methods, such as Raman spectroscopy or X-ray diffraction, which are only able to characterise a small surface fraction of the pieces, whereas RS may be highly modified by surface effects. As a non-destructive residual stress analysis method, neutron diffraction is the preferred method for the measurement of bulk residual strains and stresses, with unique deep penetration, high spatial resolution, three-dimensional mapping capability and volume averaged bulk measurements characteristic of the neutron beam.

1.2 Objectives

The objective of this research is the determination of the residual stress field and mechanical properties in a series of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ (alumina/tetragonal ZrO_2 stabilized with 3 mol% Y_2O_3) ceramic composites. These composites (a popular ceramic system with high strength and toughness due to the typical (*t-m*) transformation toughening), are manufactured using a new tape casting route, which involves the stacking of green ceramic tapes at room temperature and using low pressures. The use of a low content of organic additions was better than the traditional manufacturing methods for producing laminated materials, both from the economic and environmental point of view. Superior mechanical properties are anticipated, as well as an unknown residual stress field originated by the pressing procedure followed to stacking the tapes together, even if tapes with the same composition are used to manufacture the ceramic structure. Little experimental data supporting these hypotheses has yet to be published. In order to take full advantage of the novel tape casting method in the future production of alumina-zirconia laminated materials, it is useful to investigate the mechanical performance and residual stresses by comparison to the materials produced by conventional slip casting. Different Y-TZP contents (5 vol.% and 40 vol.%) and green processing routes (the novel tape casting and conventional slip casting) were investigated. The residual stress profiles throughout the normal and in-plane directions in ceramics bulk samples were obtained. In addition the mechanical properties were determined, which will provide essential information on the effect of the manufacturing technique, the reinforcement volume fraction and the grain size on properties and RS development on $\text{Al}_2\text{O}_3/\text{Y-TZP}$ ceramic composites. It also gives a verification and

comparison with previous work. The understanding of the effect of green processing on the properties of ceramics is crucial to differentiate processing from compositional effects in order to develop new materials with improved mechanical properties, to be used both for thermal insulation of motors and turbines and as bioceramics in implant applications.

1.3 Structure of the thesis

- **Chapter 2** gives an introduction of residual stresses studies (e.g. definition, classification, origins, measurement techniques, theory basis of diffraction measurement, stress calculation and diffraction profile analysis), and a brief description the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ ceramics system, in terms of the characteristic, manufacturing process and some published results on mechanical performance and discussion on toughening mechanism. This chapter also discusses the previous work relating to residual stresses and its effect on mechanical properties of ceramics.
- The experimental techniques used in this thesis are presented in **Chapter 3**. It includes measurements of density, microstructure, mechanical properties (elastic modulus, hardness, flexure strength and fracture toughness) and residual stresses. In addition to the traditional measurement methods, nanoindentation technique was also used as a complementary measurement for elastic modulus and hardness. Two kinds of neutron diffraction techniques (constant-wavelength and time-of-flight neutron diffraction) were used for through-thickness residual stresses measurements in bulk materials.
- **Chapter 4** presents the determined mechanical properties of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ ceramics. Comparisons between the results by different methods were made. The toughening mechanism was discussed.
- **Chapter 5** gives the results of residual stresses in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ ceramics, by both of constant-wavelength (CW) and time-of-flight (TOF) neutron diffraction. Through-thickness residual stresses profiles were presented. Comparison between RS from single peak analysis by CW technique and those from whole diffraction profiles analysis using the TOF technique was conducted. In addition, phase quantities were evaluated by Rietveld refinement in the TOF measurement. At the end of this chapter, the contribution of RS on

mechanical properties, e.g. fracture toughness and strength, is theoretically discussed and compared with the experimental work.

- An overview of the important conclusions drawn from this study, and some recommendations and suggestions for future work, are presented in *Chapter 6*.

Chapter 2

Literature Review

2.1 Residual stresses

The engineering properties of materials and structural components, notably fatigue life, distortion, dimensional stability, corrosion resistance, and brittle fracture can be considerably influenced by residual stresses [3]. Indeed, in many cases where unexpected failure has occurred, this has been due to the presence of residual stresses which have combined with the service stresses to seriously shorten component life. Such effects are usually expensive in repairs and the restoration of parts, equipment, and structures. On the other hand, these stresses can be advantageous and sometimes be introduced deliberately, as in shot peening which is used to improve fatigue resistance, and the toughening of glass/ceramics. Accordingly, residual stress analysis is a compulsory stage in the optimizing design of parts and structural elements and in the estimation of their reliability under real service conditions. Currently, the residual stresses are one of the main factors determining the engineering properties of materials, parts, and welded elements, and should be taken into account during the design and manufacturing of different products. Although substantial progress has been achieved in the development of techniques for residual stress management, considerable effort is still required to develop efficient and cost-effective methods of residual stress measurement and analysis as well as technologies for the beneficial redistribution of residual stresses.

2.1.1 Definition and classification

The term “residual stress” describes any stress which remains in a body after manufacture and processing in the absence of external forces or thermal gradients [4]. Every material has locked-in stresses. Residual stress measurement techniques invariably measure strains rather than stresses, and the residual stresses are then calculated using the appropriate material parameters such as Young's modulus and Poisson's ratio. Often only a single stress value is quoted and the stresses are implicitly assumed to be constant within the measurement volume, both in the surface plane and through the depth, which is not true.

Following a length scale perspective, residual stresses can be defined as either macro or micro stresses and both may be presented in a component. Macro residual stresses are often referred to as Type I residual stresses, and micro residual stresses, which result from differences within the microstructure of a material, can be classified as Type II or III. Micro residual stresses often result from the presence of different phases or constituents in a material. They can change sign and/or magnitude over distances comparable to the grain size of the material under investigation.

To summarize, residual stresses can be classified as [4, 5]:

- **Type I:** refers to residual stresses which are homogeneous on a macroscopic scale (much larger than the grain size of the material) along at least one direction
- **Type II:** describes the mean deviation from the macroscopic residual stress level of an individual crystallite (single phase material). These stresses vary over the grain scale (characteristic length $l_{0,II} \approx$ grain size); may be expected to exist in single phase materials because of anisotropy between neighboring grains, and in multi-phase materials as a result of the different elastic and thermal properties of the different phases.
- **Type III:** represents the local deviation of the residual stresses within an individual crystallite from its average residual stress (characteristic length $l_{0,III} <$ grain size), e.g. variation on the atomic scale. They exist within a grain, essentially as a result of coherency at interfaces, dislocations and other crystalline defects (e.g. voids, solute atoms).

Fig. 2.1. Categorization of residual stresses according to length scales in a two-phase material.

The different types of residual stress in a two-phase material are shown schematically in **Fig. 2.1**, illustrating how these different types of stress equilibrate over different length scales. For a two phase material, the macrostress is continuous across phases, but the type II and III stresses are not. As a result, even when the sampling area is greater than the characteristic areas for type II and type III, non-zero phase-average microstresses $\langle \sigma_{\alpha} \rangle^{\text{II;III}}$ and $\langle \sigma_{\beta} \rangle^{\text{II;III}}$ for phases α and β can be recorded.

When comparing results from different techniques, consideration should be given to the sampling volume and resolution of each measurement method in relation to the type of residual stress being measured, particularly when the Type II and III micro residual stresses are of interest. The concept of the characteristic volume should be understood, over which a given type of residual stress averages to zero. If the measurement sampling volume is greater than the characteristic volume, then the stress will not be recorded. For example, most material removal techniques (e.g. hole drilling, layer removal) remove large volumes of material over which Type II and III stresses average to zero so that only the macro residual stresses can be measured. While in diffraction experiments, with the higher resolution, a non-zero volume averaged (α) phase microstress $\langle \sigma_{\alpha} \rangle^{\text{II}}$ or grain stress $\langle \sigma_{\text{hkl}} \rangle^{\text{II}}$ can be recorded superimposed on the phase independent macrostress $\langle \sigma \rangle^{\text{I}}$. Considerable

care must be taken when selecting the most appropriate residual stress measurement technique.

Generally, type I residual stresses are the most important from an engineering point of view, while the remainder are of interest in materials science studies.

2.1.2 Causes of residual stresses

Residual stresses are generated during most manufacturing processes involving material deformation, heat treatment, machining or processing operations that transform the shape or change the properties of a material. They are originated from a number of sources and can be present in the unprocessed raw material, introduced during manufacturing or arise from in-service loading [4-6].

It is possible to classify the origin of residual stresses in the following way:

- Mechanical
- Thermal
- Chemical

Mechanically generated residual stresses are often a result of manufacturing processes that produce non-uniform plastic deformation. They may develop naturally during processing or treatment, or may be introduced deliberately to develop a particular stress profile in a component.

On a macroscopic level, thermally generated residual stresses are often the consequence of non-uniform heating or cooling operations. Coupled with the material constraints in the bulk of a large component this can lead to severe thermal gradients and the development of large internal stresses. Microscopic thermally generated residual stresses can also develop in a material during manufacture and processing as a consequence of the coefficient of thermal expansion (CTE) mismatch between different phases or constituents.

The chemically generated stresses can develop due to volume changes associated with chemical reactions, precipitation, or phase transformation. Chemical surface treatments and coatings can lead to the generation of substantial residual stress gradients in the surface layers of the component.

2.1.3 Residual Stress Measurement Techniques

During the past years many different methods for measuring the residual stresses in different types of components have been developed. Measurement techniques can be divided into destructive and non-destructive ones. Regarding the non-destructive methods, they include the diffraction methods (e.g. X-ray or neutron diffraction) and others. In this dissertation, the diffraction methods were introduced in a detailed way.

2.1.3.1 Destructive techniques

The destructive techniques, also called the mechanical method, are dependent on inferring the original stress from the displacement incurred by completely or partially relieving the stress by removing material. These methods rely on the measurement of deformations due to the release of residual stresses upon the removal of material from the specimen. Sectioning, contour, hole-drilling, ring-core and deep-hole drilling are the main destructive techniques used to measure residual stresses in structural members.

2.1.3.2 Diffraction methods

Diffraction methods, as non-destructive measurements, are based on determining the elastic deformation which will cause changes in the interplanar spacing, d , from their stress-free value, d_0 . Then, the elastic strain could be calculated by using Bragg's law and stresses can be determined with the adequate elastic constants.

The most common diffraction methods are as follows.

1) Laboratory X-ray diffraction method

X-Ray diffraction methods of residual stress determination basically measure the angles at which the maximum diffracted intensity take place when a crystalline sample is subjected to X-rays. From these angles it is possible to obtain the interplanar spacing of the diffraction planes using Bragg's law. The locations of the peaks enable the user to evaluate the stress within the component.

With a relatively low wavelength ($\lambda \approx 0.1\text{--}0.2$ nm wavelength), laboratory X-rays can only probe a very thin surface layer (a few micrometers). It is limited to the non-destructive residual strain measurement of the sample surface. In-depth studies

can be conducted combined with some form of layer removal technique, but then the method becomes destructive.

Several experimental methods can be used to evaluate the stresses within a material using this diffractometer technique, including: the two-exposure method, parallel-beam method, $\sin^2\psi$ method, side-inclination method, etc. The most popular method is the $\sin^2\psi$ method. It has the advantage that inclined measurements are made at a number of angles ψ rather than at only one. Values of the lattice spacing, d , or 2θ are plotted against $\sin^2\psi$, and the stress σ_ϕ is derived by fitting the experimental data.

One of the major disadvantages with XRD is the limitation imposed on the test piece size and geometry. The geometry has to be such that an X-ray can both hit the measurement area and still be diffracted to the detector without hitting any obstructions. Problems may also occur if the surface is too rough, so the condition of the surface is a consideration. Size may also be a problem, because the entire component must fit into the diffractometer.

Laboratory X-ray diffraction has a spatial resolution typically between 1mm and tens of micrometers and a penetration depth of around 10-30 μm , depending on the material and source.

2) Synchrotron

Synchrotrons, or hard X-rays, provide very intense beams of high energy X-rays (20 – 300 keV) that are over a thousand times more penetrating than conventional X-rays. Very fast data acquisition times (<1 s) using small lateral gauge dimensions (>20 μm) at large penetration depths (as much as 50 mm in aluminum) are possible. It means that synchrotron diffraction is capable of providing high spatial resolution, three-dimensional maps of the strain distribution to millimeter depths in engineered components.

At least three different methods have been applied to date using: (i) traditional $\theta/2\theta$ methods [7], (ii) high energy two-dimensional diffraction [8], (iii) energy dispersive method [9].

In all cases, the relatively high energies involved lead to very low scattering angles, typically ranging from about 10° at moderate energies (25 keV) to about 4° at high energies (80 keV). This leads to gauge volumes having an elongated diamond shape (typically as little as 20 μm lateral to the beam, but as much as 1 mm along it) and hence poor resolution perpendicular to the scattering vector.

3) Neutron Diffraction

Neutron diffraction for residual stress measurements on industrial components is a growing field. The neutron diffraction method measures strain directly through changes in the lattice spacing as in X-ray diffraction, and is essentially unaffected by other sample properties such as texture. It has the advantage over X-rays that very large penetration depths could be accessed by neutrons, which makes them capable of measuring at near surface depths of around 0.2 mm down to bulk measurements with many centimeters (e.g. up to 100 mm in aluminum or 25 mm in steel). With high spatial resolution, neutron diffraction can provide complete three-dimensional strain maps of engineered components. This is achieved through the translational and rotational movements of the component.

With the capacity for collecting large quantities of data (via position sensitive detectors) over the whole surface and depth (depending on the thickness of the sample), neutron diffraction becomes a particularly useful technique for the validation of theoretical and numerical models for stress evaluation. Studies have been made on turbine blades for the aeronautics industry, on brazed or welded assemblies, on pieces of composite materials, thick coatings, steel and aluminum sections, etc. However, compared to other diffraction techniques such as X-ray diffraction the relative cost is much higher and the availability very much lower.

There are two kinds of sources available for neutron diffraction: steady-state nuclear reactors (continuous source) and the pulsed sources, which respectively correspond to two neutron diffraction techniques, namely, conventional $\theta/2\theta$ scanning (constant-wavelength method) and time of flight approaches (TOF).

- **Steady state reactor (Constant-wavelength neutron diffraction)**

For the continuous source (reactor), a monochromatic incident beam (λ fixed) is generally used with a conventional $\theta/2\theta$ scanning, also called constant-wavelength (CW) neutron diffraction. A typical diffractometer for elastic scattering on a steady state source includes a crystal monochromator, collimators, a goniometer for the sample and single or position-sensitive detectors (**Fig. 2.2 a**).

This technique is similar to the X-ray diffraction method. Lattice spacings d_{hkl} are determined from the measured angular position ($2\theta_{hkl}$) of the diffraction peak hkl by illuminating the specimen with constant wavelength neutrons diffraction, following Bragg's law. Shifts $\Delta\theta_{hkl}$ in a single hkl diffraction peak are monitored, and elastic strains are given by:

$$\varepsilon_{hkl} = \frac{d_{hkl} - d_{hkl}^0}{d_{hkl}^0} = \frac{\Delta d_{hkl}}{d_{hkl}^0} = -\cot \theta_{hkl}^0 \Delta \theta_{hkl} \quad (2.1)$$

where θ_{hkl}^0 is the angle at which Bragg peak is observed from the strain free reference, d_{hkl}^0 is the strain-free lattice spacing and d_{hkl} is the stressed lattice spacing.

It is more conventional to use a scattering angle of $\pi/2$ since this gives a cuboidal gauge volume. In principle the whole diffraction profile could be obtained by constant-wavelength neutron diffraction scanning, but then different peaks would correspond to different strain directions. Thus, it is usual for the lattice strain, ε_{hkl} , for a single peak hkl to be measured. An example of an individual Bragg peak from a continuous source based diffractometer is shown in **Fig. 2.2 b**. This approach is well-suited to macrostress mapping in cases where one or more individual representative peaks can be identified.

The constant-wavelength neutron diffraction instruments are available at many facilities worldwide including at the ILL (SALSA), Grenoble [10], Berlin & Munich, Czech Republic, Chalk River, Canada, USA.

Fig. 2.2. (a) Conventional monochromatic two theta scanning as practiced at a constant flux source; the strain is measured in the direction of the Q vector. (b) Example of a Bragg peak from a reactor (continuous source) based diffractometer fitted with a Gaussian distribution.

- **Pulsed sources (Time-of-flight neutron diffraction, TOF)**

Instruments on pulsed sources generally use a polychromatic (“white”) neutron beam. It is generally based on TOF techniques (**Fig. 2.3 a**). The diffraction profile is not collected as a function of the Bragg angle θ , rather being recorded as a function of time of flight (*tof*) at a fixed scattering angle 2θ (usually $\sim 90^\circ$) and the incident wavelength λ varied. The time-of-flight, t_{hkl} , at which a peak hkl is recorded, is proportional to the lattice spacing, d_{hkl} . Thus, in terms of the *tof* shift at the recorded peak, Δt_{hkl} , the strain can be given by $\varepsilon_{hkl} = \Delta d_{hkl} / d_{hkl}^0 = \Delta t_{hkl} / t_{hkl}^0$, where d_{hkl}^0 is the strain-free reference lattice spacing, t_{hkl}^0 is the strain-free reference *tof* at hkl peak.

The entire diffraction pattern is recorded and all Bragg peaks are measured simultaneously in TOF techniques (**Fig. 2.3 b**). The peaks can be fitted individually, or collectively using a Rietveld refinement [11]. This method is favorable when information from several Bragg peaks is required (textured or multiphase samples).

Examples of TOF instruments include ENGIN-X at ISIS [12], POLDI on SINQ Switzerland, SMARTS at Los Alamos and VULCAN at SNS.

Fig. 2.3. (a) Schematic of a typical pulsed source based time-of-flight instrument for strain measurement. The strain is measured in the direction of the Q vector. (b) A typical time-of-flight diffraction pattern.

2.1.3.3 Other non-destructive methods

Except of the diffraction methods, there are several other non-destructive methods, based on measurements of electromagnetic, optical and other physical phenomena in the residual stress zone. The common methods among this category are ultrasonic methods, magnetic and electrical methods, piezo-spectroscopic, Photoelastic methods and thermoelastic methods, etc. They have been introduced in detail in the literature [4, 13-16].

According to the above, considering the spatial resolution, penetration, reliability as well as the destructive (or non-destructive) effects (**Fig. 2.4**), neutron diffraction methods are preferred for through-depth strain/stress determination in present work. Thus, the following sections related to the stress determination and data analysis are specific to neutron diffraction data.

Fig. 2.4. Schematic indicative of the approximate current capabilities of the various techniques for residual stresses measurement.

2.1.4 Theory basis of diffraction measurement

2.1.4.1 Diffraction principle: the Bragg law

When a crystalline material is illuminated with a x-ray or neutron beam of wavelength λ , a diffraction pattern is observed at angle $2\theta_{hkl}$. The inter-planer spacing d_{hkl} can be determined from the angle $2\theta_{hkl}$ at which the reflection is observed, using the Bragg equation:

$$2d_{hkl} \sin \theta_{hkl} = \lambda \quad (2.2)$$

Fig. 2.5 shows a schematic illustration of Bragg scattering with angle 2θ .

Fig. 2.5. Schematic illustration of Bragg scattering.

2.1.4.2 Diffraction peak and Residual stress

Diffraction peak is mainly characterized by three parameters: peak position, peak intensity and peak shape (width). Related to residual strain/stresses research works, the diffraction peak shift and peak broadening (also called line broadening) are the most important characteristics.

- **Peak shift**

The effect of homogeneous strain that over the scale of grain size leads to a shift in the Bragg peaks (Fig. 2.6 b). The associated stresses usually correspond to both the type I and the average type II for the particular grain set. For example, in multiphase composite materials or single-phase plastically deformed alloys where strains vary from grain to grain because of elastic incompatibilities of grains in a polycrystalline aggregate. Most of the residual stresses works have to do with peak shift. A detailed stress determination procedure is described in the next section (section. 2.1.5).

- **Peak broadening (line broadening)**

Except for the peak shift, if the strain field is varying spatially at distances in the order or smaller than the grain size, associated with dislocations, point defects, and extended defects, such as stacking and twin faults, following the Eq. (2.2), different parts of the material diffract at slightly different angles, thus producing a broadened profile (Fig. 2.6 c).

Important information can be obtained from the analysis of the peak profile, such as the size of the coherently diffracting domain and to its local micro-strain distribution (type III strains). However, till now, little neutron work has been carried out in this field. It might due to the high requirement of data collection as well as the complexity of analysis, for example, the selection of right peak shape model, removing the instrumental contribution as well as the separation of size and strain effects. A detailed introduction of line broadening analysis is given in section 2.1.6.1.

Fig. 2.6. Diffraction peak profile for (a) zero strain (no macrostrain and no microstrain), (b) (compressive) macrostrain and/or type II strain, (c) microstrain.

2.1.5 Stress determination by diffraction

The diffraction methods of determining stress are based on the measurement of the interplanar spacing ($d(\phi, \psi)_{hkl}$) for various directions of the scattering vector defined by the ψ and ϕ angles (**Fig. 2.7**).

Fig. 2.7. Stress and strain components in the direction of the scattering vector given by the tilt angles (ψ, ϕ) at a measurement point (x, y, z) in the specimen co-ordinate system.

As mentioned previously, the lattice spacings (d-spacings) along the direction normal to the lattice planes (hkl) in a scattering volume can be determined from the peak position $2\theta_{hkl}$, following Bragg's law. The average elastic lattice strain, $\varepsilon_{\phi\psi}(hkl)$, in the direction of the scattering vector defined can therefore be determined by the diffraction peak shift, in terms of the deviation in the lattice spacing $d(\phi, \psi)_{hkl}$ relative to the stress-free lattice spacing d_{hkl}^0 , as:

$$\varepsilon_{\phi\psi}(hkl) = \frac{d(\phi, \psi)_{hkl} - d_{hkl}^0}{d_{hkl}^0} \quad (2.3)$$

It is possible to calculate the mean stress in the detected volume provided the relevant elastic constants for the material are known. The conversion from elastic strain to stress is given by Hooke's law:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \quad (2.4)$$

where C_{ijkl} is the stiffness tensor.

In general, shear strains cannot be measured directly by diffraction method, and full determination of the strain tensor requires measurements of the elastic strain in at least six independent directions. The strain $\varepsilon_{\phi\psi}(hkl)$ is related to the stresses through:

$$\begin{aligned}
\varepsilon_{\phi\psi}(hkl) &= \frac{d(\phi,\psi)_{hkl} - d_{hkl}^0}{d_{hkl}^0} \\
&= \frac{1}{2} s_2(hkl) \left[\begin{aligned} &(\sigma_{xx} \cos^2 \phi + \sigma_{yy} \sin^2 \phi + \sigma_{xy} \sin 2\phi) \sin^2 \psi + \\ &(\sigma_{xz} \cos \phi + \sigma_{yz} \sin \phi) \sin 2\psi + \sigma_{zz} \cos^2 \psi \end{aligned} \right] \\
&+ s_1(hkl)(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})
\end{aligned} \tag{2.5}$$

where diffraction elastic constants (s_1 and $\frac{1}{2}s_2$) are required, which can be calculated using polycrystalline elasticity models, with $\frac{1}{2}s_2(hkl) = (1 + \nu_{hkl}) / E_{hkl}$ and $s_1(hkl) = -\nu_{hkl} / E_{hkl}$. E_{hkl} and ν_{hkl} are the elastic modulus and Poisson's ratio associated with an specific reflection (hkl). The hkl specific diffraction elastic constants (DECs) provide a relationship between the elastic lattice strains and macroscopic stress.

In many cases, the main stress directions can be deduced by symmetry arguments and thus only three strain values (ε_{xx} , ε_{yy} , ε_{zz}) are required to calculate the main stresses (σ_{xx} , σ_{yy} , σ_{zz}):

$$\sigma_{xx}^{hkl} = \frac{E_{hkl}}{1 + \nu_{hkl}} \varepsilon_{xx}^{hkl} + \frac{E_{hkl} \nu_{hkl}}{(1 + \nu_{hkl})(1 - 2\nu_{hkl})} (\varepsilon_{xx}^{hkl} + \varepsilon_{yy}^{hkl} + \varepsilon_{zz}^{hkl}) \tag{2.6}$$

$$\sigma_{yy}^{hkl} = \frac{E_{hkl}}{1 + \nu_{hkl}} \varepsilon_{yy}^{hkl} + \frac{E_{hkl} \nu_{hkl}}{(1 + \nu_{hkl})(1 - 2\nu_{hkl})} (\varepsilon_{xx}^{hkl} + \varepsilon_{yy}^{hkl} + \varepsilon_{zz}^{hkl}) \tag{2.7}$$

$$\sigma_{zz}^{hkl} = \frac{E_{hkl}}{1 + \nu_{hkl}} \varepsilon_{zz}^{hkl} + \frac{E_{hkl} \nu_{hkl}}{(1 + \nu_{hkl})(1 - 2\nu_{hkl})} (\varepsilon_{xx}^{hkl} + \varepsilon_{yy}^{hkl} + \varepsilon_{zz}^{hkl}) \tag{2.8}$$

For plane stress or plane strain conditions, a further reduction to two directions is possible.

As demonstrated previously, the diffraction peak shift can be attributed by both type I and type II stresses. Therefore, it is possible to determine both macro (type I) and micro stresses (type II) in composite materials.

In a two-phase polycrystalline composite, the grains belonging to different phases have different physical and elastic properties and hence, the type II stresses averaged over one phase are not equal to zero. The mean value of stress calculated

over one phase is called the phase stress ($\bar{\sigma}^{\text{ph}}$) and it can be subdivided into the following terms with the formalism proposed by Clyne and Withers [17, 18]:

$$\sigma_{ij}^{\text{ph}} = \bar{\sigma}_{ij}^{\text{I}} + \sigma_{ij}^{\text{phE}} + \sigma_{ij}^{\text{phTh}} + \sigma_{ij}^{\text{phPl}} \quad (2.9)$$

where the superscript I is used for the macro (type I) stress, and the mismatch stresses of elastic, thermal and plastic are denoted by E, Th and Pl, respectively. In composites, the lattice strains corresponding to each phase can be determined independently using diffraction peaks with different scattering angles 2θ .

The mismatch stresses (sum of elastic, thermal and plastic mismatch stresses) are defined as the average value of the type II stresses over all grains belonging to one phase; for both phases of the material the type II stresses must add up to zero over a large volume of material. Thus, it can be obtained:

$$\bar{\sigma}_{ij}^{\text{I}} = f \bar{\sigma}_{ij}^{\text{ph1}} + (1 - f) \bar{\sigma}_{ij}^{\text{ph2}} \quad (2.10)$$

where the f is the volume fraction of phase 1.

The overall macrostress is simply the summation of two stress terms characteristic of each phase in the material. Some theoretical models (Eshelby or auto-consistent) can be used to complete this evaluation.

2.1.6 Diffraction profile analysis

Diffraction spectra are obtained after diffraction measurement and data collection. It needs to be analyzed by means of the appropriate profile fitting methods and profile shape models. Based on the good fitting of the experimental diffraction profiles, a wealth of reliable information might be extracted [19]: e.g. peak position changes due to type I (macroscopic) and type II (intergranular) strain/stresses, the amount and distribution of the phases in the material, compositional inhomogeneity, the crystallite size and shape distributions, the crystallographic orientation distribution function, the concentrations and distributions of crystal defects such as vacancies, dislocations, stacking and twin faults, etc.

2.1.6.1 Origin of the diffraction line profile

The observed (measured) diffraction profile $h(x)$ is mainly contributed by the convolution of sample $f(x)$ and instrument $g(x)$ effects, in the real mathematical and signal treatment sense [20]. The background $b(x)$ and noise $n(x)$ might also be introduced (not described here in detail).

$$h(x) = f(x) \otimes g(x) + b(x) + n(x) = \int f(y)g(x-y)dy + b(x) + n(x) \quad (2.11)$$

where x and y variables define the angular position of each measured point of the profile and have the same dimensions as 2θ , or as the reciprocal used variable.

1) Instrumental contribution— $g(x)$

The instrumental resolution function $g(x)$ is the result of the convolution of the different aberration profile contribution, purely geometrical (beam divergence, optical misalignments, deviation from punctuality of the source, collimator slit widths, etc.), or physical (like the emitted spectral width and distribution of the incident radiation). Generally, the $g(x)$ function is experimentally accessible by measuring a standard powder sample.

2) Sample contribution— $f(x)$

Using high resolution diffractometers, it is possible to observe the deviation of observed profile $h(x)$ from instrumental contribution $g(x)$ due to sample microstructure. This deviation in line broadening is called physical broadening, and essentially it comes from two effects:

- i) Size broadening: Broadening due to the finite size of crystallites. The simplest analysis of this broadening, developed from Scherrer equation [21], gives:

$$\beta(2\theta) = \frac{K\lambda}{D \cos \theta} \quad (2.12)$$

in which D is the mean size of the diffraction crystallites for the diffraction selected by θ , and K is the Sherrer dimensionless constant, close to unity, which depends in the crystallite shape.

- ii) Strain broadening: broadening due to crystallite microdistortions. It is defined by the crystallite non-uniform variations of d_{hkl} , which can be produce by

external stresses, crystalline defects (dislocations for instance) or local compositional variations (in solid solutions for instance). It can be shown that:

$$\beta(2\theta) = 4e \tan \theta \quad (2.13)$$

where e is the relative non-uniform deformation of the interreticular distance. Notably, a strain broadening effect can be observed even if the macrostrain (mean value of the strain distribution) is zero.

The size and strain broadening effects might be present simultaneously and can also exist individually. The analysis of line broadening is interesting for the purpose of extracting information about crystallite size and structure imperfections. The analysis is always complex and appropriate line broadening models are needed. Several related methods are proposed. Roughly, they can be divided into two types: phenomenological ‘top–bottom’ approaches, such as integral-breadth methods (summarized by Klug & Alexander [22]; see also by [23]) and Fourier methods [24–26].

Simplified integral-breadth methods that assume either Gaussian or Lorentzian function for a size and/or strain-broadened profile were shown to yield systematically different results [27]. Nowadays, it is widely accepted that a ‘double-Voigt’ approach, that is, a Voigt-function approximation for both size-broadened and strain-broadened profiles [23, 28–31] is a better model than the simplified integral-breadth methods. This model also agrees with the Warren–Averbach [25] analysis on the assumption of Gaussian distribution of strains [31, 32].

Despite the attempts to assess systematic differences between results obtained by different line-broadening methods, generally comparison is difficult because of the different definition of parameters and procedures.

2.1.6.2 Modelling/Fitting methodology

Several diffraction profile fitting methods are available [33–35]. If one single or several non-overlapping peaks are measured, single peak fitting can be carried out and parameters can be determined for each peak separately. If a diffraction pattern is measured over a wide range of peaks, the analysis of the whole spectrum using, for example, Rietveld [11], Pawley [34] or Le Bail [36] profile methods, can be performed, while single peak fitting would also be possible. Among these, the most widely used refinement method in neutron diffraction is the Rietveld Refinement [11], due to its powerful and reliable ability in the separation and extraction of

information even from overlapped peaks. It has originally been developed for monochromatic (constant-wavelength) neutron diffraction analysis, and has been extended to monochromatic x-ray experiments [37] and modified to allow time-of-flight neutron diffraction [38] and x-ray energy dispersive data analyses. A review of present day methods for diffraction line profile analysis can be found in Ref [19].

2.1.6.3 Parameters and mathematic functions for profile fitting

A number of parameters should be considered in the process of diffraction data analysis, including: peak position, peak shape, peak width, scattering background, peak amplitude, etc. Taking the aforementioned origin of the diffraction line profile into consideration, different mathematic functions and information are introduced according to the diffraction instrument used (e.g. radiation source, geometry, slit sizes) and sample information (e.g. domain size, stress/strain, defects).

- Background function (e.g. constant, linear interpolation or polynomial functions)
- Profile Shape Functions (e.g. Gaussian, Lorentzian, pseudo-Voigt function, Pearson VII[37], split Pearson VII [39], parameterized pseudo-Voigt [40], split-type pseudo-Voigt [41], etc.)
- Profile parameters (e.g. peak width FWHM, peak asymmetry, and 2θ correction, etc.)
- Sample effects (unit-cell parameters, absorption, crystal structures and restraints, size and strain broadening, etc.)
- Preferred orientation correction (if texture existed)

2.1.6.4 Reliability of results

With the good fitting of experimental diffraction profiles, peak position can be determined. The fitting algorithm should also provide an estimate of the statistical error of the peak position, which determines the statistical error of the strain measurement ($\Delta d/d$).

The quality of the fitting can also be given numerically. For instance, in Rietveld method the least-square refinements are carried out. A number of criteria-of-fit (R values) are developed to judge how well the refinement proceeds and to assess the quality of the final fit.

Table 2.1. Criteria-of-fit in Rietveld refinement

Criteria of fit	Definition
"R-pattern", R_p	$R_p = \frac{\sum y_{oi} - y_{ci} }{\sum y_{oi}}$
"R-weighted pattern", R_{wp}	$R_{wp} = \left[\frac{\sum w_i (y_{oi} - y_{ci})^2}{\sum w_i y_{oi}^2} \right]^{1/2}$
"Goodness of fit", GOF	$R_{wp} = \left[\frac{\sum w_i (y_{oi} - y_{ci})^2}{N - P + C} \right]^{1/2}$
<p>The subscript i denotes all points in the pattern range undergoing refinement. y_{oi} is the observed intensity at the i^{th} data point y_{ci} the calculated intensity at the i^{th} data point $w_i = 1/y_{oi}$ is the weight assigned to each observed intensity N= the number of observations P = the number of refined parameters C = number of constraints applied</p>	

2.1.7 Software implementation

Many programs have been developed to treat diffraction data more efficiently, flexibly and reliably. A summary of the diffraction software is given both in the literature [42] and websites. The common ones are listed here: GSAS [43], MAUD [44], Fullprof [45], TOPAS [46] and Topas Academic [47], etc.

Most of these programs allow both single peak and full pattern analysis by Rietveld and other codes. Diffraction data can be x-ray (constant-wavelength and energy-dispersive), neutron (constant-wavelength and time-of-flight) diffraction data. Visual interfacing and easy handling of most functionality are generally allowed in these programs. The selection of programs depends on the type of diffraction data, the fitting methods as well as the information sought and analysis focus.

2.2 Al₂O₃/Y-TZP ceramics system

Alumina-zirconia ceramics have received considerable attention in both engineering and academic fields due to their improved mechanical properties compared with pure alumina ceramics [48-51]. As one of the most popular alumina-zirconia materials, the alumina (α -Al₂O₃)/Y-TZP (tetragonal zirconia polycrystalline stabilized with 3 mol.% Y₂O₃) exhibit desirable performance, e.g. high strength and toughness as well as excellent biocompatibility, wear resistance, high chemical and corrosion resistance, and it is regarded as a strong candidate for structural and biomedical applications [1, 2]. Great interest is put on the possible reinforcing mechanisms as well as the influential factors, which can be closely associated to the processing route, as well as the addition of the appropriate zirconia content.

2.2.1 Materials characteristic

2.2.1.1 Alumina

Alumina is one of the most versatile of refractory ceramic oxides and it forms the basis for a large group of ceramic materials. With the high melting point (2054°C), high chemical inertia and considerable hardness and elastic modulus ($H_v \approx 18$ GPa, $E = 400$ GPa, for materials with a high density $> 99\%$ of theoretical density), which are even maintained at high temperatures [52, 53], alumina materials are used in different structural applications at both room temperature and high temperatures. Alumina-based products currently have more than 50% of the total world market for technical ceramics [54]. However, although with a relatively higher fracture toughness K_{IC} ($\sim 3\text{-}4$ MPa m^{1/2} [52, 53]) compared with conventional porcelains and other single oxide ceramics, the problems of alumina are presented in structural applications due to their relatively low defect tolerance, inclination to abnormal grain growth (AGG) [55, 56] and hence related deterioration [52, 57, 58] in mechanical properties. Therefore, the introduction of dopants or secondary phase [59-61] to enhance alumina has always been necessary. A summary of typical properties for alumina at room temperature is given in **Table 2.2**.

2.2.1.2 Zirconia

Zirconia is characteristic to its polymorphic crystal structure, with three typical structural forms: monoclinic (m), tetragonal (t), and cubic (c) [62, 63]. Pure undoped exhibits the following phase transformations (Fig. 2.8) [64]:

Fig. 2.8. Schematic representation of phase transformations between the three polymorphs of ZrO₂ and their corresponding space groups: (a) cubic ($Fm\bar{3}m$), (b) tetragonal ($P4_2/nmc$), and (c) monoclinic ($P2_1/c$). [65]

The transformations between different polymorphs are important for the processing and mechanical properties (strength, toughness, etc.) of zirconia ceramics. It has been well documented in the literature [63, 66-69] that the tetragonal to monoclinic (t→m) transformation in pure undoped zirconia during cooling is a reversible thermal martensitic transformation, associated with a large temperature hysteresis (around 200 °C for undoped zirconia) and a finite amount of volume change (4–5%). This leads to crumbling of the sintered part made from pure zirconia. Several dopants (yttria, ceria, magnesia, calcia etc.) can be added to stabilize the high temperature t and/or c-phase in the sintered microstructure. Among of them, yttria (Y₂O₃) dopant as a stabilizer in the zirconia phase has been widely used [64, 70-72]. The incorporation of Y₂O₃ into the zirconia structure was determined as Y substituting randomly for Zr, accompanied by a charge-compensating number of vacancies on the O-atom site. The overall Y-content and Y-distribution has a significant influence on the transformation toughness of ceramics. With the optimum

values of 3 mol% of Y_2O_3 being added, the zirconia tetragonal phase can be retained at room temperature from the sintering temperature (tends to be 1400 to 1600 °C), which can produce very fine-grained ceramics (0.2-1microns) and obtain high fracture stress (≈ 1 GPa). The 3 mol% Y_2O_3 -stabilized tetragonal zirconia polycrystal is called Y-TZP here. The control of t $\rightarrow$ m transformation in sintered zirconia materials is desirable to enhance properties in general.

In the bulk form, zirconia exhibits some desirable properties, notably high elastic modulus and hardness, a high melting point, and outstanding corrosion resistance [6]. The microstructure can also be engineered such that relatively high fracture toughness can be generated. Some typical properties for a commercial Y-TZP are listed in **Table 2.2**.

Table 2.2. The overview of properties of alumina and Y-TZP materials.

Properties	Materials	
	Al_2O_3	Y-TZP
Density (g/cm^3)	3.99 *	6.10 **
Elastic Modulus, (GPa)	393 [73]	210 [76]
	387-440 [74]	200-210 [73]
	378-431 [75]	221 [77]
Poisson's ratio	0.22 [76]	0.31[76]
	0.22-0.24 [74]	
Thermal Expansion Coefficient, (range of 20-1200 °C) ($10^{-6} \text{ }^\circ\text{C}^{-1}$)	8.6 [78]	10.8 [79]
Vickers Hardness, (GPa)	13-17 [74]	12-13 [73, 76]
	18.3 [80]	12.7 [80]
Flexure Strength (MPa)	330-430 [74]	800-1500 [73, 76]
	360-412 [81]	880-1275 [83]
	310 [82]	800-1000 [82]
Fracture Toughness ($\text{MPa} \cdot \text{m}^{1/2}$)	3-4 [74]	7-12 [76]

*: Materials (Al_2O_3) with density (> 98% T.D.) and grain size of 1-6 μm ;

**: Materials (Y-TZP) with density (> 99% T.D.) and grain size 0.2-1 μm .

2.2.1.3 Alumina/Y-TZP composites

The development of alumina/Y-TZP is aimed to substitute alumina ceramics in applications where a higher fracture resistance was required, i.e. orthopedic implants.

Fig. 2.9. The phase diagram of $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system at 1450 °C

Fig. 2.9 shows the phase diagram of $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system at 1450 °C [84]. It is clear that with 3 mol% of Y_2O_3 , the materials are compatible, without phase reaction between alumina and Y_2O_3 . Addition of yttria to zirconia replaces some of the Zr^{4+} ions in the zirconia lattice with Y^{3+} ions. Y-TZP is present as the tetragonal zirconia in alumina. Both the alumina matrix and the Y-TZP dispersed phases are mutually insoluble, with no intermediate phases, and are thermally and chemically stable up to the eutectic temperature (around 1700 °C) [84].

It was reported that the existence of Y-TZP particulates in the alumina matrix could affect both the microstructure and mechanical properties of ceramics. An increase in the mechanical properties due to the presence of the zirconia phase in the alumina matrix has been observed by many works.

Tuan *et al.* [50] observed that by adding both t- ZrO_2 and m- ZrO_2 particles it can significantly enhance the mechanical properties of alumina, which reported the fracture toughness values for single-phase alumina ($\sim 3.9 \text{ MPa m}^{1/2}$) and $\text{Al}_2\text{O}_3/5 \text{ vol.}\%$ Y-TZP ($\sim 5.0 \text{ MPa m}^{1/2}$). Szatkowska [90] determined the fracture toughness values for single-phase alumina ($\sim 3.8 \text{ MPa m}^{1/2}$) and alumina/7 vol.% Y-TZP ($\sim 4.5 \text{ MPa m}^{1/2}$) materials using the single-edge-notch bending technique (SENB). For the alumina materials with 40 vol.% of Y-TZP, fracture toughness was determined by Tarlazzi *et al.* [85] and Sglavo *et al.* [86] using different measurement methods, with similar values of $4.3 \pm 0.1 \text{ MPa m}^{1/2}$ and $4.5 \pm 0.3 \text{ MPa m}^{1/2}$ obtained by chevron-

notched bending and bending with the Vickers indentation, respectively. Magnani *et al.* [99] obtained values of fracture toughness of $6.1 \pm 0.1 \text{ MPa m}^{1/2}$ for materials of 70 vol.% Y-TZP/30 vol.% alumina by the technique based on the crack length from Vickers indentation.

Casellas *et al.* [87] studied the effect of thermally induced microstructural coarsening on the fracture toughness of zirconia-alumina composites containing 5, 15 and 30 vol.% Y-TZP. The composites were cold isopressed at 200 MPa and sintered at 1,600 °C for 2 hours. It was observed that microstructural coarsening of this dual phase ZTA was dependent on the volume fraction of the second phase. At low volume fraction (5 vol. %) of Y-TZP, the grain growth of the matrix (Al_2O_3) is pinned by the dragging force of Y-TZP. However, at 10 vol.% Y-TZP, zirconia clusters are formed which becomes more effective pinning the grain boundaries. When Y-TZP addition > 30 vol.%, microstructural coarsening became difficult and Al_2O_3 grain growth was absent due to large volume of ZrO_2 which prevent grain to grain contact of Al_2O_3 . The increase in fracture toughness with Y-TZP addition was correlated to transformation toughening effect.

Weimin *et al.* [88] studied the densification behavior, microstructure and transformation behavior of Al_2O_3 -2YTZP (2 mol% Y_2O_3 -stabilized tetragonal zirconia) and Al_2O_3 -3YTZP composites (3 mol% Y_2O_3 -stabilized tetragonal zirconia), which contained 10, 15, 20, 25, 30 vol. % of Y-TZP. The volume fraction of Y-TZP affected the t→m ZrO_2 transformation. At 15 vol% Y-TZP addition, the composites sintered to near theoretical density. Energy spectrum analysis confirmed a different bonding level of Al^{3+} with 3Y-TZP and 2Y-TZP. High toughness values were obtained at Y-TZP level 15-20 vol% with transformation toughening being the predominant mechanism.

From all the above it indicates that the properties of the alumina-zirconia ceramics can be varied depending on the addition of Y-TZP to activate various microstructural strengthening/toughening mechanisms.

2.2.2 Powder processing: Colloidal processing

The mechanical properties of ceramics depend critically on the quality of the microstructure, e.g. uniform distribution of zirconia particles and homogeneous microstructures, which in turn are strongly predetermined by processing routes [89]. Manufacturing a ceramic product requires a systematic that provides adequate

control of each of the stages to be established since the properties of the compound at each stage all remaining determined.

Most advanced ceramics are formed as powder compacts and densified by sintering. Powder processing generally involves five basic steps (2): (i) powder production, (ii) preparation of powders for consolidation, (iii) consolidation to an engineering shape (or called forming into shape), (iv) removal of solvent and organic additives (drying and burnout), and (v) densification. An optimized powder processing route of sufficient quality can eliminate heterogeneities from the powders, and ensure minimum density variation and small scale of the residual flaw population and absence of large scale porosity/flaws in the final material (e.g. after the final sintering). Colloidal processing techniques have been successfully applied to make green bodies of ceramics with improved product reliability, which involves the manipulation and control of the interparticle forces in powder suspensions, in order to remove heterogeneities and to optimize the suspension properties. There are many reports in the literature regarding colloidal processing of alumina-zirconia. Suzuki *et al.* [90] studied the dispersion behavior of Al_2O_3 - ZrO_2 suspension and observed that additional redispersion treatment such as ultrasonication helps to produce dispersed suspension by preventing the agglomeration tendency of fine particles. Compacts prepared from ultrasonicated suspension exhibited more than 55% elongation as a result of extremely fine and uniform microstructure resulting from colloidal processing. Ramakrishnan *et al.* [91] noticed that due to the difference in pH range of stability of Al_2O_3 and ZrO_2 , their mixed suspension exhibited heterocoagulation. Experimental results indicated while the zirconia suspension is stable either below pH 6 or above pH 8. For mixed suspension of Al_2O_3 - ZrO_2 , the suspension is unstable between pH 7 and 9. Novak *et al.* [92] correlated the electrokinetic properties of ZrO_2 to the rheology and microstructure of Al_2O_3 - ZrO_2 suspensions. It was proposed that washing/ageing of the ceramic particles prior to suspension making is expected to improve the dispersion and densification as well as the sintered microstructure.

Different forming methods are included in the colloidal processing techniques, e.g. tape-casting [93, 94], centrifugal casting [95, 96], sequential slip casting [97-99], electrophoretic deposition (EPD) [100, 101], and others. All of them are based on the preparation of stable slurries with specific compositions that are piled up by adding a layer to a previously formed one. Stable slurries that ensure a homogenous and well-dispersed composition are obtained by controlling the interparticle potentials developed within the liquid media [102, 103]. The thickness is controlled by controlling the processing parameter associated to the technique (casting time [97,

104], blades gap [105], amount of slurry [98], etc.), which can be taken advantage of in the manufacture of laminated materials.

Among of these, tape casting is very attractive and more extensively used, especially for producing multilayer ceramics, due to its suitability for mass production and its flexibility for different layered structures design (e.g. composites, thickness, stacking sequence). Comparing it with the monolithic composites manufactured by conventional slip casting methods, better mechanical behavior was anticipated in the direction perpendicular to the constituent layers in specimens made from individual tapes [106-108].

Traditionally, the tapes are manufactured with thermoplastic binders and plasticizers in an organic media and pressed at a temperature close to the melting temperature (20–120 °C) of the tape additives. Nowadays, the tendency in production methods is to use water-based formulations, for economic reasons as well as in order to avoid environmental and safety problems derived from the use of organics [48–50]. Unfortunately, the use of water-based systems for tape casting makes tapes to be more prone to cracking during drying, because of the evaporation of water is slower than that of organics. In order to overcome this problem, the optimization of the slurry in terms of high solid content is required. A high solid content reduces the amount of water to be evaporated and, consequently the tendency of the tape to cracking [48]. J. Gurauskis *et al.* [93, 109] have proposed a novel tape casting route for stacking green ceramic tapes made from water-based slurries at room temperature and using low pressures, which could overcome the disadvantage (like anisotropy and high porosity) in traditional tape casting processing due to a high content of organic additives, and also establish the optimum conditions to obtain defect-free sintered materials.

As discussed above, different processing methods might introduce a remarkable difference in the materials' properties. It is crucial to make a careful selection of processing routes for developing advanced ceramics like the laminate ceramics, in order to meet the enhanced requirement in the application. In addition, knowledge of the effect caused by the green processing on the properties of the materials is critical to differentiate effects due to processing and due to the design (composition, thickness and distribution). This would allow more control over the design of new materials with improved properties.

2.2.3 Toughening mechanisms in the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ system

As regards the improved mechanical properties by the addition of Y-TZP into the alumina matrix, the possible toughening mechanisms in the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials system are summarized at below:

i) Stress-induced phase transformation toughening

Fig. 2.10. Schematic showing the stress-induced phase transformation of metastable tetragonal zirconia particles in the crack tip stress field. The arrows indicate the generation of compressive residual stress due to the transformation-induced volume expansion and the microstructural constraint.

It is known that the metastable tetragonal zirconia transformation toughening refers to the phenomenon that t- ZrO_2 inclusions, which are dispersed in the alumina ceramic matrix, and undergo a phase transition to the stable monoclinic symmetry in the tensile stress field around a propagating crack [110-112]. The concomitant volume expansion (4–5%) involved in this phase transition introduces a net compressive stress in the process zone around the crack tip. This essentially reduces the local crack tip stress intensity factor as well as the driving force for crack propagation. The net result is an increase in the toughness (see **Fig. 2.10**).

The critical stress intensity factor (fracture toughness) of a brittle multiphase material, K_{Ic} , is commonly described by a relationship of the form:

$$K_{Ic} = K_0 + \Delta K_c \quad (2.13)$$

where K_0 is the matrix toughness and ΔK_c the contribution from various crack-shielding mechanisms. The mechanism of transformation toughening can be described by a change in the stress intensity factor. A great deal of intellectual

energy has been expended in attempting to devise theories and develop mathematical frameworks to model the mechanism [113-116]. The important parameters that influence the transformability of t-ZrO₂ as well as the transformation toughening effect [117] are summarized as, e.g. grain size, grain shape, grain boundary phase, yttria content and yttria distribution, MS temperature, transformation zone size and shape, residual stress, etc.

ii) Microcracking toughening

Fig. 2.11. Microcrack toughening induced in the zirconia ceramics as a result of the formation and the subsequent growth of microcracks, as a consequence of stress-induced t-ZrO₂ phase transformation in the process zone.

Microcracks in zirconia-toughened ceramic materials can be subdivided into residual microcracks and stress induced microcracks [118, 119]. The residual microcracks are due to the volume expansion and shear strain associated with the tetragonal-monoclinic transformation which takes place on cooling from the sintering temperature. The stress induced microcracks are those caused by the volume expansion and shear strain associated with the subsequent stress-induced transformation during fracture process [120]. It is considered that residual stresses are required for the formation of stress-induced microcracks; however, the magnitude of the stresses is insufficient to cause spontaneous microcracks. Thus when the external stress and the tensile stress associated with the tetragonal-monoclinic transformation are linearly superimposed on the residual stresses, microcracks will be induced. Microcracks around a primary crack can increase toughness through the dissipation of crack tip stress as they grow and by their interaction with the crack tip stress field. These effects reduce the local stress concentration at the crack tip, giving rise to primary crack tip shielding and resultant toughening of the matrix. It is considered to be one of the most commonly occurring

toughening mechanisms in alumina-zirconia. However, the presence of microcracks leads to a reduction in stiffness (effective elastic modulus).

iii) Crack deflection

Evans *et al.* [113, 121] considered that cracks can be deflected by localized residual stress fields which are developed as a result of phase transformation, thermal expansion mismatch or by the fracture of a second phase. The deflection results in a degree of toughening dictated by the reduced force on the deflected portion of the propagating crack. For the deflection by a second phase in the matrix, the parameters which have been shown to influence the toughening include volume fraction, particle morphology and aspect ratio of the second phase.

iv) Internal residual stresses

The internal residual stresses, which generate during the cooling process from sintering temperature, might be another important resource for toughening in alumina-zirconia system. Such thermal residual stresses mainly arise due to two factors: (a) the thermal expansion mismatch (CTE mismatch) between the Y-TZP phase and the Al_2O_3 matrix ($\alpha_{\text{A},25-1000^\circ\text{C}}=8.6\times10^{-6} \text{ }^\circ\text{C}^{-1}$ [78], $\alpha_{\text{Y-TZP},25-1000^\circ\text{C}}=10.8\times10^{-6} \text{ }^\circ\text{C}^{-1}$ [79]), and (b) the anisotropy thermal expansion (CTE anisotropy) in a single phase, e.g. for $\alpha\text{-Al}_2\text{O}_3$ ($\alpha_{\text{a},25-1000^\circ\text{C}}=8.4\times10^{-6} \text{ }^\circ\text{C}^{-1}$, $\alpha_{\text{c},25-1000^\circ\text{C}}=9.2\times10^{-6} \text{ }^\circ\text{C}^{-1}$) [78], for the t- ZrO_2 phase ($\alpha_{\text{a},25-1000^\circ\text{C}}=10.06\times10^{-6} \text{ }^\circ\text{C}^{-1}$, $\alpha_{\text{c},25-1000^\circ\text{C}}=11.6\times10^{-6} \text{ }^\circ\text{C}^{-1}$) [79]. literature [122] reported that in a $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (CeO_2) system, tensile residual stresses were generated in zirconia (CeO_2 -doped) grains and compressive ones were in the Al_2O_3 matrix.

The residual stress is reported to be an important parameter in optimizing the toughness of Y-TZP-contained materials. Numerous investigations [79, 123, 124] have probed the influence of residual stresses on the transformability of the t- ZrO_2 phase and the toughness of ceramics. Based on x-ray measurements, Krell *et al.* [125] reported a residual stress of 20–60 MPa in 3Y-TZP ceramics with grain sizes in the range of 0.5–1.0 μm . Finite element modeling (FEM) calculations showed that higher CTE anisotropy in 2Y-TZP results in larger residual stress as well as increased transformability and subsequently enhanced toughness [126]. Also, CTE mismatch ($\alpha_{\text{c}}/\alpha_{\text{a}}$) varies commensurately with the tetragonality (c/a) of t- ZrO_2 and a transition is reported to take place at about 4.5 mol% yttria with stabilization of the cubic structure [127]. Grain size and cracking levels were modified due to the existent RS.

Even though several research works have been carried out on the residual stresses analysis of alumina-zirconia system, however, due to the difference in manufacture processing, composition design, and the measurement techniques, remarkable variances are observed. It is crucial to use a reliable measurement technique and to look into the residual stresses carefully.

2.3 Present Investigation

According to the overview above, the microstructure and mechanical properties of the alumina-zirconia composites can be optimized with the addition of Y-TZP and processing techniques. The residual stresses, as anticipated due to the thermal expansion mismatch and anisotropy in alumina-zirconia systems, can also be affected by the Y-TZP content and processing techniques. Considering the toughening mechanisms, residual stresses effect should be emphasized and carefully analysed, with the use of appropriate measurement techniques. In this work, neutron diffraction, both the constant-wavelength and time-of-flight neutron diffraction techniques, have been used for reliable through-thickness residual strain measurement in bulk samples. Stresses were precisely determined, by combining appropriate analysis methods, e.g. the single peak fitting and Rietveld refinement. The phase compositions in sintered ceramics especially those of zirconia were accurately examined by Rietveld analysis, considering the complex polymorph of ZrO_2 and the possible phase transformation during the manufacture process.

The novel tape casting method [93, 109], which involved the stacking of green ceramic tapes at room temperature and using low pressures, is selected for investigation, in order to take full advantage of the future development of alumina-zirconia laminated materials. Features of materials obtained by the new processing method are determined and compared with those of materials obtained by conventional slip casting in a plaster mold, in order to analyze whether the proposed method of processing affects the microstructure and thereby the mechanical properties. To analyze the adequacy of the manufacturing process used to avoid the presence of discontinuities at the interfaces between the sheets and other phenomena that interfere with the mechanical properties, ceramic materials with the same composition in tapes were produced and investigated.

Moreover, the effect of the addition of Y-TZP in composites was also studied, in order to meet the requirement of co-sintering of layers with a different composition in laminated materials. The effects of Y-TZP content and the new

processing method on the microstructure, mechanical performance and residual stresses were summarized in the currently studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials. The toughening mechanisms, especially the residual stresses related toughening, were theoretically discussed.

Chapter 3

Experimental Work

3.1 Introduction

A characteristic type of alumina-based ceramic composites, $\text{Al}_2\text{O}_3/\text{Y-TZP}$ (alumina/tetragonal ZrO_2 stabilized with 3 mol% Y_2O_3), was studied in this thesis, which were prepared in the Instituto de Cerámica y Vidrio, CSIC, Spain.

The methods and techniques used for the manufacturing processing, microstructure and mechanical characterization, and residual stress measurement and analysis are detailed in the following sections.

3.2 Materials preparation

Two compositions, 95 vol. % of $\alpha\text{-Al}_2\text{O}_3$ with 5 vol. % of Y-TZP (named A-5YTZP) and 60 vol. % of $\alpha\text{-Al}_2\text{O}_3$ with 40 vol. % of Y-TZP (named A-40YTZP), were selected for investigation. Two kinds of green processing methods were used in the manufacture of each composition: the novel tape casting [93, 109] which involved the stacking of green ceramics tapes at room temperature and using low pressures, and the conventional slip casting, as a reference route. The studied specimens were

named as A-5YTZP(slip), A-5YTZP(tape), A-40YTZP(slip) and A-40YTZP(tape), in order to describe compositions and manufacturing techniques.

The materials to be studied were prepared using high-purity α - Al_2O_3 (Condea HPA-0.5, USA, $d_{50}=0.35 \mu\text{m}$, specific surface area: $9.5 \text{ m}^2/\text{g}$) and polycrystalline tetragonal zirconia stabilized with 3 mol. % Y_2O_3 (TZ-3YS, TOSOH, Japan, $d_{50}=0.4 \mu\text{m}$, specific surface area: $6.7 \text{ m}^2/\text{g}$), named Y-TZP, as the starting powders. The properties of starting powders are listed in **Table 3.1**. In addition, XRD analysis of the raw powders was conducted by the materials supplier in previous work [128]. It was reported that only the α - Al_2O_3 phase was detected in the alumina starting powder. In zirconia starting powder, there were about 70 vol.% of Y_2O_3 -stabilized tetragonal zirconia (*t*) phase and 30 vol.% of monoclinic zirconia (*m*) phase, as diffraction profiles presented in **Fig. 3.1**.

Table 3.1. The properties of raw powders used for $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites

Powder	Provider	Purity	Specific surface area (m^2/g)	Average particle size (μm)	Others
α - Al_2O_3	Condea, USA	99.8	9.5	0.35 (d_{50})	Spherical in shape
Zirconia (TZ-3YS)	TOSOH, Japan	-	6.7	0.4 (d_{50})	3 mol% Y_2O_3

Fig. 3.1. XRD analysis of the raw powders used for $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites [128]. a) the starting Al_2O_3 powder (Condea HPA-0.5, USA); b) the starting zirconia powder (TZ-3YS, TOSOH, Japan), including 70 vol.% of Y_2O_3 -stabilized tetragonal zirconia (*t*) and 30 vol.% of monoclinic zirconia (*m*).

Stable slurries were prepared by mixing the starting powders with 47 vol. % of solid content in deionized water, using a polyelectrolyte (Dolapix CE 64, Zschimmer and Schwarz, Germany) as dispersant. Slurries were ball milled for 4 h using alumina jar and balls. One series was manufactured by slip casting the deflocculated suspensions in plaster mould and leaving them to dry for 24 h. The other series was manufactured by tape casting on a polypropylene film using a moving tape-casting device with two doctor blades using a 10 mm/s casting velocity and a 500 μm gap height between the blades and the carrier film. After tape casting, the green ceramic tapes were dried at room temperature for 24 h and subsequently at 60 °C degrees for 48 h. A water-based polymeric emulsion Mowilith DM 765 E (Celanese, Tarragona, Spain), with solid content 50 vol. %, particle size 0.05-0.15 mm, was used as the binder emulsion. The final thickness of the green tapes varied between ~480 μm to 520 μm . A monolithic piece was prepared by stacking 11 layers of the same compositions taped together and by applying a gluing agent (5 wt. % dilution in distilled water of the binder) under uniaxial pressure of 18 MPa at room temperature. A detailed description of the green processing and pressing procedure is given elsewhere [93, 109].

All the green samples were machined into bars (approximately 40 mm×40 mm×5 mm) and the surfaces were smoothed with sandpaper. For binder burnout, green bodies were pre-sintered at 600 °C for 30 min, with a heating rate of 1 °C/min. Subsequent sintering was carried out at maximum temperature of 1500 °C, with a dwell of 2 h (heating and cooling rates of 5 °C/min).

3.3 Characterization of sintered materials

3.3.1 Density

The densities of all the sintered samples were measured at room temperature, based on the Archimedes principle with distilled water as the immersion medium (European Standard EN 1389:2003), using a Mettler Toledo ME-33360 density determination kit.

The bulk density, ρ , and the percentage value of open porosity, ϕ , was calculated by (Eqs. 3.1 and 3.2.):

$$\rho = \left(\frac{M_D}{M - M_S} \right) \cdot \rho_{\text{water}} \quad (3.1)$$

$$\phi = \left(\frac{M_S - M_D}{M - M_S} \right) \cdot 100 \quad (3.2)$$

where M_D is the dry mass, M is the mass of the specimen saturated with water, M_S is the mass of the specimen suspended in water, and ρ_{water} is the density of the water at the measurement temperature.

Relative densities were calculated as a percentage of the calculated theoretical density for each composition, using 3.99 g/cm³ for α -Al₂O₃ (ASTM 42-1468) and 6.10 g/cm³ for Y-TZP (ASTM 83-113). For monolithic compositions the value of theoretical density, ρ_{theor} , was calculated using the law of mixtures and the volume percentage of each phase:

$$\rho_{\text{theor}} = \rho_A \cdot V_A + \rho_i \cdot V_i \quad (3.3)$$

where ρ_A and V_A is theoretical density and volume percentage of α -Al₂O₃ phase respectively, and ρ_i and V_i is theoretical density and volume percentage of the second phase Y-TZP, according to the studied composites. At least 6 measurements were taken for each material to obtain the average values, with the standard deviation as error.

3.3.2 Microstructure Characterization

3.3.2.1 Sample Preparation

The general sequence of sample preparation for microstructural characterization begins with cutting specimens 5×5×5 mm³. The cutting is performed on cutting instrument (Struers OPAL 460, Germany), using a diamond-impregnated circular disc of 0.4 mm thickness, with a low rotation speed of the disc (100 rpm) and small weights (150 g) to minimize potential damage of the sample surface.

The cut samples were mounted in resin (Epofix-EPOES, Struers, Denmark), and then be ground with silicon carbide paper from P400 to P1200. The ground samples were carefully polished using diamond suspension from 6, 3 to 1 μm on nylon cloth, until a mirror-like surface was obtained. An automatic polishing

machine (Labopol-5, Struers, Copenhagen, Denmark) was used throughout the sequence of grinding and polishing, with a rotation speed of 150 rpm and an applied force of 15-20 N.

Chemical etching was performed on the polished samples to reveal the grain boundaries and facilitate observation in the electron microscope, without inducing new stresses in the material. For A/Y-TZP composites, 85% H_3PO_4 was used for 7 min at 200°C.

3.3.2.2 Optical Microscopy

The reflected light optical microscopy, Axiovert 100A-Zeiss, Germany, was used to observe the evolution of the different stages of polishing and for a first evaluation of the final appearance of materials.

In addition, the observation of the imprints produced in the Vickers indentation test, as well as the measurements of indentation cracks length, was performed by this technique.

3.3.2.3 Scanning Electron Microscopy

For microstructure characterization and grain size determination, the scanning electron microscopy (SEM) was used on the polished and chemical etched surfaces of the sintered materials.

Fracture surface characterizations were performed by scanning electron microscopy on the fractured samples after the bending test (section 3.3.3.4), for the determination of the fracture mechanism and understanding the toughening mechanism of materials.

The fracture surfaces prepared for SEM examination were previously metallized to make them conductive, by means of vacuum deposition of a gold layer using a HITACHI E-1030 sputter coater operated at 15 mA for 30 s.

3.3.2.4 Grain Size

The average grain size (d_{50}) for each phase in materials was determined on the SEM micrographs through the linear intercept method of Fullmann [129], using the

correction factor $4/\pi$. At least 200 grains for each phase were considered for each studied materials.

3.4 Mechanical Testing

3.4.1 Elastic modulus

The elastic modulus, E , describing the stiffness of material, is one of the most important properties of solid materials. For reliable determination of the elastic modulus E , both the dynamic and static methods were used in this work:

- 1) The dynamic method, based on measurement of the resonance frequency of the material pieces, was conducted with impulse excitation of vibration, following the standard set out in ASTM E-1876. For each monolithic material, four samples (with geometry of $20 \times 5 \times 2 \text{ mm}^3$) were analyzed to obtain the average value of measurements. From the detected frequencies, dimensions and densities of the samples, the values of elastic modulus (E), the shear modulus (G) and Poisson's ratio (ν) were calculated.
- 2) The static method was conducted using three-point bending test on the rectangular bar samples. The sintered monoliths blocks of A/Y-TZP samples were machined into $25 \times 5 \times 2 \text{ mm}^3$ for the bending test.

The three-point bending test was conducted on a universal testing machines (Instron Corp., Instron 5866, USA) with a cross-head at a speed of 0.1 mm/min and with the inner span set to 16 mm for A/Y-TZP materials system. The flexure loading configurations was depicted in **Fig. 3.2**, in which the loading direction was parallel to the planes of the stacking tapes in the tape casting samples in A/Y-TZP materials system. For the slip casting samples, considering the manufacturing process (green processing and sintering) without pressure, the bulk samples were assumed as isotropic.

Fig. 3.2. Schematic arrangement of sample in a three-point bend test. The loading direction was parallel to the planes of stacking tapes in the tape casting samples in A/Y-TZP materials system.

Engineering stress (σ)–strain (ε) curves were calculated from the load values and the displacement of the central part of the samples recorded during the bending tests, using the following equations:

$$\sigma = \frac{3L_s P}{2BW^2} \quad (3.4)$$

$$\varepsilon = \frac{6\delta W}{L_s^2} \quad (3.5)$$

where L_s (mm) is the length of the support span, B (mm) is width of specimen bar, W (mm) is thickness of specimen bar, P is applied load (N), δ is the value equal to the displacement of the loading arm.

The static Young's modulus, E , was determined from the slope of the initial linear part of the stress–strain curves, as:

$$E = \frac{L_s^3}{4BW^3} \frac{\Delta P}{\Delta \delta} \quad (3.6)$$

3.4.2 Flexural strength

The flexural strength, σ_f , was determined by three-point bending test on the rectangular bar samples (geometry of $20 \times 5 \times 2 \text{ mm}^3$), under conditions of a span length of 16 mm and a constant loading speed of 0.5 mm/min.

The flexural strength (σ_f) was calculated using the following equations:

$$\sigma_f = \frac{3L_s P_{\max}}{2BW^2} \quad (3.7)$$

where L_s is the length of the support span (mm), $P_{\max}$ is the applied maximum load (N), B is the width of specimen bar (mm), W is the thickness of specimen bar (mm).

For each material, three samples were prepared for the bending test to obtain an average value and the standard deviation.

3.4.3 Hardness

The determination of hardness (H_V) was conducted on the polished samples by means of Vickers indentation (LECO V-100-C hardness tester), with a load of 100 N for a dwell time of 15 s. For each sample, at least 10 indentations were used to obtain the average values and standard deviation.

Optical microscopy was performed on the indented samples, and the diagonal of the indentation and crack length was measured. Vickers hardness (H_V) was determined by equation below:

$$H_V = 1.854 \frac{P}{d^2} \quad (3.8)$$

where P is the applied load, d is the average length of the diagonals of the indentation impression.

3.4.4 Fracture toughness

Fracture toughness (K_{Ic}) values are used extensively to characterize the fracture resistance of ceramics and brittle materials. The fracture of brittle ceramics is usually controlled by the mode I fracture toughness. Many methods are developed to evaluate the fracture toughness of ceramic materials and method selection can be material and resource dependent [130-133]. During fracture toughness testing, a known flaw (e.g. notches or pre-cracks) is introduced into the material for the determination of fracture energy, which is required to be reliable, reproducible and avoid introducing unwanted damage, in order to create accurate test results. Due to the intrinsic brittle characteristics, ceramics are generally highly sensitive to flaws and the measurements of fracture toughness of ceramics are complicated. Therefore, it's crucial and to select a proper method to introduce the notches or pre-cracks.

In this work, fracture toughness (K_{Ic}) of A/Y-TZP materials was evaluated by two different methods: (i) the Single Edge Laser-Notch Beam (SELNB) method [134-136] and (ii) the indentation fracture (IF) method [137, 138].

1) The Single Edge Laser-Notch Beam (SELNB) method, introducing an ultra-sharp V notch by laser assisted-machining in a bending bar, was conducted under the three-point bending test.

It was reported that the fracture toughness results of this single-edge-notch beam test were very sensitive to notch shape and geometry (notch tip radius, width and depth) [139]. In the common single-edge-V notched beam (SEVNB) [140, 141] test, the notching way is normally carried by scribing using a razor blade and diamond suspension, where the notch precision especially the achievable tip radius is constrained by the thickness of the blade used for notching. This can be problematic for fracture toughness testing in brittle materials, because when the root radius of the notch is larger than relevant microstructural features the fracture toughness results will be adversely affected by the size effect [139, 142]. The fracture toughness values are shown to vary with the square root of the radius until a critical root radius is achieved [143, 144]. The introduction of very sharp notches on specimens is essential for accurate testing. Previous studies [134] confirmed the advantages that laser notching can be more economical than conventional mechanical methods and can also produce notches with minimal unwanted damage to the surrounding material for fracture toughness testing of ceramics. Due to this reliability in the notch size, this method is recommended for notching ceramics or other brittle materials.

Fig. 3.3. View of the sharp Laser-V-notch on the investigated specimens.

For this study, considering the effect of tip radius of notch on K_{Ic} determination, as well as the difficulties in machining notch on demanded radius and length and without introducing other unexpected thermal damage and cracks for brittle ceramics, infrared ultra-short laser pulses were utilized to create a sharp Laser-V-notch on bar specimens. Prior to implementation, the laser working conditions were optimized to obtain the sharpest notch root radius together with minimal thermal damage. For all the samples in present work, the notch was sharpened up to a radius of less than $5\ \mu\text{m}$ to minimize the influence of notch radius on K_{Ic} [140]. The final depth of the starting notch was between $90\ \mu\text{m}$ and $120\ \mu\text{m}$. Laser notching was shown to produce notches that have a consistent geometry with no noticeable unwanted damage around the notch, as illustrated in **Fig.3.3**.

After the notching process, the Laser-notched bar specimens with geometry of $20\times5\times2\ \text{mm}^3$ were tested on a universal testing machine (Instron Corp., Instron 5866, USA) at room temperature, with a span length of 10 mm and a constant displacement rate of 0.1 mm/min. The load and load point displacement were continuously monitored using a load cell and a linear variable differential transformer induction transducer, respectively. Note that the loading direction was parallel to the planes of the stacking tapes in the tape casting samples. The experimental set-up as well as the schematic arrangement of the Laser-notched sample in test was shown in **Fig.3.4** and **Fig.3.5**, respectively.

Fig. 3.4. Experiment set-up in SELNB test.

Fig. 3.5. Schematic arrangement of laser-notched beam sample in SELNB test.

For each material, three specimens were tested to determine the average value of K_{Ic} . The following expression was used for K_{Ic} calculation [145]:

$$K_{Ic} = \frac{3L_s P_{\max}}{2BW^{3/2}} \cdot \alpha^{1/2} \cdot Y^* \quad (3.9)$$

$$Y^* = \frac{(1.989-0.356\beta)-(1.217+0.315\beta) * \alpha + (3.212+0.705\beta) * \alpha^2 - (3.222+0.02\beta) * \alpha^3 + (1.226-0.015\beta) * \alpha^4}{(1-2\alpha)(1-\alpha)^{1.5}}$$

where: P_{max} is the applied load at fracture, L_S is the length of the support span, B is width of specimen bar, W is thickness of specimen bar, a is V-notch depth, Y^* is the stress intensity shape factors, $\alpha = a/W$, $\beta = W/L_S$.

Fracture surface characterizations were performed by scanning electron microscopy on fractured samples after SELNB test.

2) The indentation fracture (IF) method, based on the Vickers indentation test, was used for the determination of fracture toughness, as a comparison with the SELNB method. This method is much easier to conduct and without the need for the preparation of the specimens with special geometry and complex notches. Only a small volume of material was required to conduct the microfracture indentation K_{IC} measurements.

The Vickers indentation test was carried on a polished specimen surface with a Vickers microhardness tester using a load of 100 N for a dwell time of 15 s. At least 10 indentations were used for each sample to obtain the average values and standard deviation. Optical microscopy was performed on the indented samples, with a measurement of the diagonal of the indentation ($2a$) and the crack length ($2c$) which emanate from the corners of Vickers indentation diagonals (**Fig. 3.6**).

The determination of fracture toughness (K_{IC}) in indentation fracture (IF) method depends on the types of crack system, which were generally classified into two modelling: the Palmqvist model and the half-penny/Median model. Different sub-structures were exhibited from these two models, as shown schematically in **Fig. 3.6** (a) and (b), where the form of median (half-penny) cracks completely surround the indentation (**Fig. 3.6** b), and the Palmqvist cracks begin only at the end of the diagonals of the indentation (**Fig. 3.6** a).

Fig. 3.6. Top and cross-sectional views of the crack formation through Vickers indentation. (a) the Palmqvist crack model and (b) the half-penny/Median crack model.

Various theoretical models were developed for the determination of indentation fracture toughness in brittle materials, according to the crack model. In present work, the theoretical models proposed by Nihara *et al.* [20] and Shetty *et al.* [21] were used for fracture toughness calculation for Palmqvist cracks system, and the ones of Laugier *et al.* [22] and Anstis *et al.* [14] were used for median (or half-penny type) cracks, as presented in **Table 3.2**.

Table 3.2. Selected formulas used for calculation of indentation fracture toughness.

Model	Authors	Formulas used for calculation of K_{IC} [MPa·m ^{1/2}]
Palmqvist Cracks $c/a < 2.5$	Nihara <i>et al.</i> [146]	$K_{IC} = 0.0122P / (al^{1/2})(E / H_V)^{2/5}$
	Shetty <i>et al.</i> [147]	$K_{IC} = 0.0319P / (al^{1/2})$
Median cracks (half-penny) $c/a > 2.5$	Anstis <i>et al.</i> [138]	$K_{IC} = 0.016(E / H_V)^{1/2} (P / c^{3/2})$
	Laugier <i>et al.</i> [148]	$K_{IC} = 0.01(E / H_V)^{2/3} (P / c^{3/2})$

* where P is the applied load in Vickers indentation test, E is the measured Young's modulus, H_V is the measured Vickers hardness, a is the half-diameter of the indented section, c is crack length measured from the centre of indent to the crack tip, l is the crack length, $l = c - a$.

The identification of the crack model was done by two methods:

- (i) The empirical way according to the ratio of cracks-to-indent size (c/a) at sample surface (top view in **Fig. 3.6**), where a is the half-diameter of the indented section, and c is crack length measured from the center of indent to the crack tip. As a general rule, it is suggested [149] that if $c/a < 2.5$, it is considered as Palmqvist model, and if $c/a > 2.5$, the crack model is considered as half-penny/Median type.
- (ii) The observation methods, which was conducted by polishing the indented sample surface down to some depth—the depth of h_1 and h_2 in **Fig. 3.6** (a) and (b), then use optical microscopy to observe the new-polished indented surface for identification. For different crack models, the new surface observation will be different.

3.4.5 Nanoindentation tests

Considering the effect of microstructure (microcracks and porosity, etc.), for reliable determination of the elastic modulus E and hardness H of the studied ceramics, nanoindentation tests were also used in this work.

The sintered samples were mounted, ground flat, and then polished carefully with a fine diamond paste to obtain a scratch-free, mirror-like surface suitable for indentation. The nanoindentation tests were performed on Nanoindenter XP (NanoInstruments Innovation Center, MTS systems, TN, USA), using a Berkovich diamond indenter with a 50 nm tip radius. The depth sensing indentations tests (DSI) were operated using the continuous stiffness measurement methodology (CSM) [150]. In CSM module, continuous loading and unloading cycles were conducted during the loading branch by imposing a small dynamic oscillation of 2 nm and 45 Hz on the displacement signal and measuring the amplitude and phase of the corresponding force [151]. Consequently, the contact stiffness can be measured continuously during the penetration depth.

Prior to nanoindentation test, the system was calibrated using a fused silica standard. The displacement-control test was conducted with a maximum penetration depth of 1,500 nm. For each sample, an array of 25 indentations in a 5×5 matrix with 50 μm spacing was performed, attempting to determine the overall (composite) response. All tests were conducted at room temperature.

Curves of applied indentation loads (P) as a function of penetration depth (h) were determined during both loading and unloading. A schematic representation of a typical data set obtained with a Berkovich indenter is presented in **Fig. 3.7** [152, 153].

Fig. 3.7. Schematic illustration of indentation load–displacement data showing important measured parameters. [152, 153]

From these curves, hardness (H) and Young's modulus (E) were extracted, as a function of the penetration depth, employing the model proposed by Oliver and Pharr [152].

The contact hardness, H_c , is defined as the ratio of the peak load, $P_{\max}$, to the contact area, A . The contact area, A , is a shape function of the contact depth, h_c , described by [152, 153]:

$$A = 24.5h_c^2 + c_1h_c^1 + c_2h_c^{1/2} + c_3h_c^{1/4} + c_4h_c^{1/8} + c_5h_c^{1/16} \quad (3.10)$$

where $c_1 \dots c_5$ are constants determined through curve-fitting procedures.

The contact depth, h_c , in the above equation is given by [152, 153]:

$$h_c = h_{\max} - 0.75 \frac{P_{\max}}{S} \quad (3.11)$$

where h_{max} is the maximum penetration depth, and S is the contact stiffness determined from the unloading curve. The unloading curve is well approximated by the following power law equation:

$$P = k_2(h - h_f)^m \quad (3.12)$$

where k_2 and m are the power law constant and exponent, respectively, empirically determined by curve-fitting procedures, h is an instantaneous indentation displacement and h_f is the final depth. The contact stiffness, S , is determined from the slope of the initial part of unloading curve, described as [152]:

$$S = \left(\frac{d_p}{d_h} \right)_{h=h_{max}} = mk_2(h_{max} - h_f)^{m-1} = \frac{2}{\beta\sqrt{\pi}} E_r \sqrt{A} \quad (3.13)$$

where β is a correction factor which was established as 1 ± 0.05 [153], E_r is the reduced modulus between the specimen and the indenter.

Once the contact area is determined, the hardness is estimated:

$$H = \frac{P_{max}}{A} \quad (3.14)$$

Young's modulus (E) of the specimen can be determined from [152]:

$$E = (1 - \nu^2) \left[\frac{1}{E_r} - \frac{(1 - \nu_i^2)}{E_i} \right]^{-1} \quad (3.15)$$

where E_i and ν_i are the Young's modulus and Poisson's ratios of indenter, respectively, which corresponds to values of 1,141 GPa and 0.07 for a diamond indenter [152]; ν is the Poisson's ratio of specimen. In present work, the Poisson's ratio ν of the studied A/Y-TZP materials was taken from the results determined by dynamic method, as introduced in section 3.3.3.1.

3.5 Residual Stresses Measurement

Information of residual stresses is very useful in the study of the microstructure of materials as well as providing important data to optimize their performance and reliability. Several non-destructive methods for residual stresses measurement were

described in Chapter 2. Determination of stresses within bulk samples requires a high energy, high flux, X-ray source such as a synchrotron or a neutron source. With the advantage of high penetration of neutron into engineering materials, neutron diffraction is considered as an optimal method for residual stresses measurement. Two kinds of neutron diffraction techniques were used for residual strain scanning in this dissertation, namely, the constant-wavelength (CW) neutron diffraction and the time-of-flight (TOF) neutron diffraction.

In this section, the experimental set-ups with the sample geometry and data collection in each technique, as well as the analysis methods and procedure, will be described.

3.5.1 Constant-wavelength neutron diffraction

3.5.1.1 Experimental set-up

Residual strain measurements were performed by constant-wavelength (CW) neutron diffraction on the strain imager SALSA (Strain Analyser for Large Scale engineering Applications) [10], at the ILL, Grenoble, France. SALSA (**Fig. 3.8**) is a monochromatic strain diffractometer (strain imager) stationed on a continuous flux neutron beam. The high penetration and delivered flux of the neutron beam makes it ideal for non-destructive measurements deep in bulk samples. In particular, it features a hexapod Stewart platform as a sample stage, which allows very flexible and precise sample handling capabilities, like tilted positions for textured samples and arbitrary scan trajectories in the 3D space. Moreover, continuously variable take-off angle and monochromator orientation give an arbitrary choice of the wavelength. Thanks to a large steel table placed beneath all components (the delta table), the wavelength change does not require any realignment.

Fig. 3.8. Overview picture of the SALSA strain scanning instrument at the ILL, Grenoble.

All the studied materials were cut and ground to obtain the test samples in this residual strain scanning. The final geometry of samples in A/Y-TZP materials system was $20 \times 20 \times 5 \text{ mm}^3$. Note that for the A/Y-TZP pieces manufactured from tape casting, the large surfaces ($20 \times 20 \text{ mm}^2$) were parallel to the surface of the stacked tapes.

In our work, the wavelength used was $\lambda = 2.06 \text{ \AA}$. The (double-focusing) Si-monochromator reflection (311) was used with a take-off angle of 85° . A 2D position-sensitive detector with an angular opening of approximately 5° was mounted on SALSA. Primary and secondary slits were used to set the gauge volume (which can be varied automatically via step motors) of $1 \text{ mm} \times 1 \text{ mm} \times 10 \text{ mm}$.

For the investigated A/Y-TZP materials system, strain scanning was respectively carried out for each phase in each sample: Al_2O_3 and Y-TZP phase. For each phase, strain scanning was performed through the whole sample thickness to obtain the strain/stress profile in bulk sample. The scan step was 0.4 mm along the whole thickness of 5 mm in A/Y-TZP materials system.

Considering the fabrication process which was utilized in this work, both slip casting and tape casting, the stress state was assumed to be isotropic in the larger plane of the sample, so that only the strains along the in-plane and the normal directions (**Fig. 3.9**) were measured. The in-plane direction, parallel to the larger plane of the samples ($20 \text{ mm} \times 20 \text{ mm}$), and the normal direction, perpendicular to it,

were assumed to be the principal stress component directions in residual stress determination.

The starting powders (the $\alpha\text{-Al}_2\text{O}_3$ and Y-TZP powders), which were used to manufacture the bulk composites, were used as strain/stress-free reference samples for residual strain/stress determination. The strain scanning of powder was conducted by holding in vanadium cans.

Precise specimen positioning was achieved by performing entrance scans. During the scanning of Al_2O_3 phase, some points well out of the specimens were measured, to check the reproducibility of the entrance curves traced on the base of the detector integrated intensity. All measurements were carried out at room temperature.

Fig. 3.9. Experimental set-up of residual stresses measurement by constant-wavelength neutron diffraction in SALSA diffractometer, both in the (a) in-plane and (b) normal directions.

It was suggested [154] that the reflections with Bragg angle of $2\theta \approx 90^\circ$ was a better choice for strain scanning which satisfies a homogenous coverage of the gauge volume while rotating the sample. Peaks with relatively high intensity and no overlap with other peaks were chosen for measurement. In A/Y-TZP materials system, both the $\text{Al}_2\text{O}_3(300)$ and the $\text{Al}_2\text{O}_3(116)$ reflections for Al_2O_3 were detected near $2\theta = 90^\circ$. As regards the Y-TZP phase, the YTZP(211) peak at $2\theta = 84.1^\circ$ was selected, which has a neighbouring peak, the YTZP(103), at $2\theta = 82.8^\circ$.

3.5.1.2 Data analysis

After strain scanning, the LAMP software [155] was used to analyze the CW experimental results and obtain the peak parameters for selected reflections.

An accurate description of the peaks' shapes in a diffraction pattern is critical to the success of profile/peak fitting and the following information extraction and analysis. The pseudo-Voigt function, as a linear combination of Lorentzian and Gaussian components, was used as a peak-shape function during fitting. The background was approximated as flat.

The peak information, e.g. peak position 2θ , intensity and full width at half maximum (FWHM), were accessed after fitting. According to Bragg's law, the lattice spacing of a given set of planes (hkl) can be evaluated by precise measurements of the diffraction peak position 2θ :

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \quad (3.16)$$

where λ is the wavelength used, $\lambda = 2.06 \text{ \AA}$, d_{hkl} is the lattice spacing of the hkl reflection, θ is half of the obtained diffraction peak position 2θ .

Thus the strain within the material can be calculated from the peak shift, corresponding to the variation of the lattice spacing:

$$\varepsilon_{hkl} = \frac{d_{hkl} - d_{hkl}^0}{d_{hkl}^0} \quad (3.17)$$

where ε_{hkl} is the longitudinal strain in the direction of the scattering vector, d_{hkl} is the obtained lattice spacing of the hkl reflection measured from bulk materials, and

d_{hkl}^0 is the unstressed lattice spacing of the hkl reflection, which is obtained from the stress-free starting powders.

3.5.2 Time-of-flight (TOF) neutron diffraction

3.5.2.1 Experimental set-up

The test samples for TOF neutron diffraction were prepared in the shape of parallelepipeds with dimensions 20 mm×20 mm×5 mm in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials system.

The time-of-flight (TOF) neutron diffraction for residual strain/stress measurements was conducted on ENGIN-X instrument, a third-generation neutron strain scanner, operating at the ISIS spallation neutron source in the Rutherford Laboratory, UK. Details of this instrument are given in [35].

Fig. 3.10. Experimental set-up on the time-of-flight neutron strain scanner ENGIN-X at ISIS. (a) residual strains were collected both in the in-plane and normal direction. (b) strain scanning was carried out along the sample thickness with the interior gauge volume.

The experimental setup consists of two detector banks which are centered on Bragg angles of $2\theta_B = \pm 90$ degrees, as shown in **Fig. 3.10**. It allows simultaneous measurements of strain in two directions: the in-plane direction, parallel to the larger plane of the samples ($20 \times 20 \text{ mm}^2$), and the normal direction, perpendicular to it, which are assumed to be the main stress component directions. Considering the geometrical symmetry in samples and the manufacturing process, the stress state was assumed to be isotropic in the larger plane of the sample, so the strains measured along the in-plane and normal directions are enough for stresses determination.

The gauge volume in measurement is defined by incident horizontal and vertical cadmium slits and a radial collimator slit in front of each detector bank. In the studied A/Y-TZP materials system, the measurement gauge volume for bulk samples was set to $15 \times 1 \times 1 \text{ mm}^3$. The centroid of this gauge volume defines the location of the measurement. Strain scanning was carried out along sample thickness (thickness of 5 mm in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ system), with measurement point interval of 0.4 mm.

The stress-free reference lattice parameters of $\alpha\text{-Al}_2\text{O}_3$ and Y-TZP (3 mol% Y_2O_3 stabilized zirconia) were obtained by measuring the $\alpha\text{-Al}_2\text{O}_3$ and Y-TZP raw powders. The gauge volume used for powder measurements was set to $16 \times 3 \times 1 \text{ mm}^3$, in order to obtain diffraction spectra with enough signal and thus to determine the stress-free reference lattice parameters accurately. The CeO_2 powder, used on the ENGIN-X instrument as an experimental standard, was measured to calibrate the peak profile parameters. All measurements were carried out at room temperature.

3.5.2.2 Data Analysis

In TOF neutron diffraction measurements, the whole diffraction patterns were obtained from each scanning point in bulk samples. The program TOPAS-Academic V5 [47] was adopted to refine the diffraction patterns.

For the refinement of time-of-flight diffraction profiles, two sets of information are critical and they need to be carefully treated: the diffractometer constants and the profile shape function. CeO_2 powder, as a highly crystalline sample which brings minimal line broadening, with space group $Fm\bar{3}m$ and cubic lattice parameter $a=5.4114 \text{ \AA}$, was used as standard sample for calibration of the instrument. Detailed refinement procedure was introduced here.

a) Diffractometer constants

Diffractometer constants, $DIFC$, $DIFA$ and $ZERO$, are very important for the calculation of TOF peak position. They are highly instrument dependent and associated to the neutron time-of-flight tof of the individual reflection and its corresponding d-spacing, d .

$$tof = DIFCd + DIFAd^2 + ZERO \quad (3.18)$$

Initial values for these constants were given in the ENGIN-X instrument parameter files and then be refined during the calibration refinement with the CeO_2 standard powder data.

Due to variation from one detector bank to another, the calibrated diffractometer constants for both detector banks were refined respectively. The relation formulas between tof (μs) and d ($\text{\AA}$), with the obtained calibrated diffractometer constants, were finally given below:

$$tof_{bank1} = 18355.6d - 4.35d^2 - 16.2 \quad (3.19)$$

$$tof_{bank2} = 18457.3d - 6.6d^2 - 22.7 \quad (3.20)$$

b) Profile function

According to the description of profile shape for TOF neutron diffraction in Larson & Von Dreele's GSAS manual [43], the TOF profile function #3 in manual was used, as a convolution of a pseudo-Voigt function $pV(t)$ with two back-to-back exponentials $E(t)$.

$$H(\Delta T) = \int pV(\Delta T - t)E(t)dt \quad (3.21)$$

where H is the profile function, ΔT is the offset of the profile point from the reflection position in tof .

The pseudo-Voigt function $pV(t)$ is a linear combination of a Lorentzian function $L(t, \Gamma)$ and Gaussian $G(t, \Gamma)$ function, expressed as:

$$pV(t) = \eta L(t, \Gamma) + (1 - \eta)G(t, \Gamma) \quad (3.22)$$

$$G(t) = \frac{1}{\sqrt{2\pi}\Gamma_G} \exp\left[-\frac{t^2}{2\Gamma_G^2}\right] \quad (3.23)$$

$$L(t) = \frac{\Gamma_L}{2\pi} \frac{1}{\left[\left(\Gamma_L/2\right)^2 + t^2\right]} \quad (3.24)$$

where η is a mixing factor of Gaussian and Lorentzian functions, and Γ_G and Γ_L are the FWHM of Gaussian and Lorentzian components, respectively.

The exponential functions, $E(t)$, depicted a asymmetric shape consisting of the sharp build-up and the slower drop-off in intensity, describing the physics of neutron production at ISIS, as below:

$$E(t) = 2Ne^{\alpha t}, \quad t \leq 0 \quad (3.25)$$

$$\text{and } E(t) = 2Ne^{-\beta t}, \quad t > 0 \quad (3.26)$$

where the normalization factor $N = \frac{\alpha\beta}{2(\alpha + \beta)}$, with d-spacing dependent coefficients $\alpha = \alpha_1 / d$, $\beta = \beta_0 + \beta_1 / d^4$.

After the instrumental calibration procedure by the standard CeO_2 powder, the obtained instrument-dependent diffractometer constants and profile parameters should be fixed and used for the following refinements of the starting powders and bulk samples.

Rietveld refinement was used for the analysis of the whole TOF diffraction profile. As a well-known whole profile structure refinement method, Rietveld refinement is powerful for determining complete crystal structures (e.g. lattice parameters, atomic coordinates, occupancy, etc.), microstructure information and the residual stresses in a multiphase material. Quantitative phase analysis can be achieved by Rietveld analysis in TOPAS software.

In Rietveld refinement, a least-squares refinement is carried out until the best fit is obtained between the observed diffraction pattern and the calculated pattern based on parameters describing the instrumental parameters, crystal structure, diffraction optics effects and other specimen characteristics.

Fig. 3.11. The TOF neutron diffraction patterns of the standard CeO_2 powder (blue line), as well as its fitting profiles (red line) by Rietveld refinement. A good fit was achieved with the weighed residual error $R_{\text{wp}}=9.6\%$.

As introduced previously, the ENGIN-X instrument diffraction profile was modeled using a convolution of a pseudo-Voigt function $pV(t)$ (a linear combination of a Lorentzian function and Gaussian function) with two back-to-back exponentials $E(t)$ [43]. Diffraction profiles of the standard CeO_2 powder, as well as its fitting profiles (red line) by Rietveld refinement, were shown in **Fig. 3.11**, representing the instrument diffraction profile. The difference plot between the observed and calculated intensities was shown in grey line, below spectra. Good fit was achieved with the weighed residual error $R_{\text{wp}}=9.6\%$. The obtained instrument-dependent diffractometer constants and profile parameters were fixed and used for refinements of bulk samples and stress-free references powders.

Variable parameters like lattice parameters, atomic coordinates, isotropic thermal parameters, scale factors and polynomial background parameters, etc. were refined during the Rietveld refinements. All the refinements were conducted step-by-step to avoid correlation [156]. The space groups and initial atomic structure information used in refinements of A/Y-TZP materials system are listed in **Table 3.3**. The overall quality of fitting was assessed in terms of R values [156], as obtained from refinement in TOPAS.

Table 3.3. Initial crystal structure parameters used in refinement for A/Y-TZP materials system.

Phase	Space group	Lattice parameter / Å	Ionic position and coordinate			
			ion	x	y	z
α -Al ₂ O ₃ [157] (hexagonal)	$R\bar{3}c$	a=b=4.7602	Al ³⁺	0	0	0.35216
		c=12.9933 $\alpha=\beta=90^\circ$ $\gamma=120^\circ$	O ²⁻	0.30624	0	0.25
Y-TZP [158] (tetragonal)	P42/nmc	a=b=3.6183	Zr ⁴⁺	0	0	0
		c=5.1634	Y ³⁺	0	0	0
		$\alpha=\beta=\gamma=90^\circ$	O ²⁻	0	0.5	0.217
m-ZrO ₂ [67] (monoclinic)	P21/c	a=5.1505	Zr ⁴⁺	0.2754	0.0395	0.2083
		b=5.2116	O ₁ ²⁻	0.07	0.3317	0.3447
		c=5.3173 $\beta=99.23^\circ$	O ₂ ²⁻	0.4496	0.7569	0.4792

3.5.3 Residual Stress determination

Residual stresses behavior can be estimated either from lattice parameters variation or individual *hkl* peaks shifts. The former represented the average stress behaviors of individual phase, named as mean phase stress, and the latter is stress in individual grain, named as peak-specific residual stresses. As summarized from above, lattice parameters were obtained from the Rietveld refinement of the TOF whole diffraction profiles, and d-spacings of individual peaks were obtained by single peak analysis from both of CW neutron diffraction and TOF neutron diffraction measurements.

3.5.3.1 Mean phase stresses

With the Rietveld refinement of the entire diffraction spectrum, lattice parameters of each phase in composites can be obtained. The mean phase strain, given by a weighted average of several single-peak strains, was determined from the change of average lattice parameters in Rietveld refinements of the entire diffraction spectrum [159]. Taking all diffraction peaks into account, it was used to represent the bulk behaviors effectively, with a more precise and reliable strain determination of the materials.

In this study, for hexagonal $\alpha\text{-Al}_2\text{O}_3$ phase, strain can be calculated along lattice axis:

$$\varepsilon_a = \frac{a - a_0}{a_0} \quad (3.27)$$

$$\varepsilon_c = \frac{c - c_0}{c_0} \quad (3.28)$$

where a ($a = b$) and c are the lattice parameters of $\alpha\text{-Al}_2\text{O}_3$ phase, and a_0 and c_0 are the stress-free lattice parameters measured from Al_2O_3 starting powder. For the tetragonal Y-TZP, strain in a ($a = b$) and c axis can be determined in the same way.

Ignoring the local variations that occur around the particles, integration is performed over randomly oriented grains in composites. Without accounting for granular anisotropy, mean phase strains in the gauge volume were calculated by averaging the strain over the unit cell, for Al_2O_3 and Y-TZP phase respectively [160]:

$$\bar{\varepsilon}_A = \frac{1}{3}(2\varepsilon_a + \varepsilon_c)_A \quad (3.29)$$

$$\bar{\varepsilon}_{Y\text{-TZP}} = \frac{1}{3}(2\varepsilon_a + \varepsilon_c)_{Y\text{-TZP}} \quad (3.30)$$

As explained above, taking into account the manufacturing process and specimen symmetry, strains in the larger plane of samples are considered isotropic. Thus, strain measured in one in-plane and normal directions are enough for stress determination, and they are used as the principal strains ε_{ii} , $i=1, 2, 3$, as

$$\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{In\text{-}plane} \text{ and } \varepsilon_{33} = \varepsilon_{Normal}.$$

Thus, mean phase stresses for each phases were determined in directions of in-plane and normal using Hooke's law, respectively, as:

$$\sigma_{In\text{-}plane} = \frac{E}{1+\nu} \bar{\varepsilon}_{In\text{-}plane} + \frac{E\nu}{(1+\nu)(1-2\nu)} (2\bar{\varepsilon}_{In\text{-}plane} + \bar{\varepsilon}_{Normal}) \quad (3.31)$$

$$\sigma_{Normal} = \frac{E}{1+\nu} \bar{\varepsilon}_{Normal} + \frac{E\nu}{(1+\nu)(1-2\nu)} (2\bar{\varepsilon}_{In\text{-}plane} + \bar{\varepsilon}_{Normal}) \quad (3.32)$$

where $\bar{\epsilon}$ corresponds to the calculated mean phase strain for each phase, given by Eqs. (3.29) - (3.30), E and ν are the bulk elastic constants of each phase. The bulk elastic constants used for the A/Y-TZP materials systems were given out in **Table 3.4**.

Table 3.4. The bulk elastic constants used for the residual stresses calculation for A/Y-TZP materials systems.

Phase	Elastic modulus, E (GPa)	Poisson's ratio, ν
α -Al ₂ O ₃	400	0.22
Y-TZP (tetragonal) [161]	210	0.31

3.5.3.2 Peak-specific residual stresses

Diffraction measurements of residual stresses are typically made by determining the position of a single diffraction peak, which relates to the strain in a particular family of grains. Due to single crystal anisotropy, the strain measured by diffraction will differ between grain families, and therefore between diffraction peaks [162]. The deviation from the average phase stress in a given grain, i.e. the intergranular type of strains, could be accessed by measuring shifts in individual diffraction peaks. The understanding of intergranular stresses is important because stress concentrations on the scale of individual grains may ultimately be important in the initiation of processes such as fatigue or failure.

For TOF instruments, at a fixed scattering angle $2\theta_B$, the lattice spacing d_{hkl} of hkl plane is obtained from the time-of-flight (*tof*) of peak position t_{hkl} [163]:

$$d_{hkl} = \frac{h}{2 \sin \theta_B m_n L} t_{hkl} \quad (3.33)$$

where h is the Plank constant, m_n is the neutron weight and L is neutron flight path length.

The peak-specific residual strain in TOF measurement, which depends on the change in lattice spacing Δd_{hkl} of hkl plane, can then be calculated in terms of the *tof* shift at the recorded peak, Δt_{hkl} .

$$\varepsilon_{hkl} = \Delta d_{hkl} / d_{hkl}^0 = \Delta t_{hkl} / t_{hkl}^0 \quad (3.34)$$

where d_{hkl}^0 is the strain-free reference lattice spacing, t_{hkl}^0 is the strain-free reference *tof* at hkl peak. Peak positions can be precisely determined by individual peak fitting, with a typical sensitivity of $\delta_\varepsilon = \Delta d_{hkl} / d_{hkl} \cong 50\mu\varepsilon$.

For both of the constant-wavelength (CW) and time-of-flight (TOF) neutron diffraction measurements, the peak-specific residual strains measured in in-plane and normal direction are differentiated as $\varepsilon_{In-plane}^{hkl}$ and $\varepsilon_{Normal}^{hkl}$, which were considered as the main strain components, as discussed in [164], taking into account the manufacturing process and specimen symmetry. Thus, strain measured in one in-plane and normal directions are enough for stress determination, and they are used as the main strains ε_{ii} , $i=1, 2, 3$, as $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{In-plane}$ and $\varepsilon_{33} = \varepsilon_{Normal}$.

The peak-specific residual stresses for each reflection of Al_2O_3 and Y-TZP in in-plane and normal directions, $\sigma_{In-plane}^{hkl}$ and σ_{Normal}^{hkl} , were calculated using Hooke's law, respectively, as below formula:

$$\sigma_{In-plane}^{hkl} = \frac{E_{hkl}}{1 + \nu_{hkl}} \varepsilon_{In-plane}^{hkl} + \frac{E_{hkl} \nu_{hkl}}{(1 + \nu_{hkl})(1 - 2\nu_{hkl})} (2\varepsilon_{In-plane}^{hkl} + \varepsilon_{Normal}^{hkl}) \quad (3.35)$$

$$\sigma_{Normal}^{hkl} = \frac{E_{hkl}}{1 + \nu_{hkl}} \varepsilon_{Normal}^{hkl} + \frac{E_{hkl} \nu_{hkl}}{(1 + \nu_{hkl})(1 - 2\nu_{hkl})} (2\varepsilon_{In-plane}^{hkl} + \varepsilon_{Normal}^{hkl}) \quad (3.36)$$

where E_{hkl} and ν_{hkl} are the diffraction elastic constants (DEC) corresponding to hkl in each related phase. In this dissertation, the DEC of $\text{Al}_2\text{O}_3(hkl)$ and Y-TZP(hkl) were obtained by program IsoDEC [165, 166], according to the Kröner model [167, 168].

3.5.3.3 Diffraction line broadening analysis

Diffraction line broadening has been observed in the TOF neutron diffraction profiles in present work. As a research focus for diffraction profile analysis, a wealth of microstructural information like domain size, crystal microstrain and crystal defects (vacancies, dislocations, stacking, etc.) are possible to be detected through line-broadening analysis. Two principal effects are generally accepted to contribute to the diffraction line broadening: instrumental response and sample physical

broadening such as microstrain (strain broadening) and small size crystallite (size broadening).

To determining accurate sample physical contribution, a correction of instrument broadening is essential and it was conducted in this work by Rietveld refinement of standard CeO₂ powder, which is assumed to have no size and strain broadening. “Double-Voigt” modelling [31, 169] was employed for describing of physical size and strain broadening, according to D. Balzar’s study [169] on size-strain line-broadening analysis and Rietveld refinement. The TOF profile model has the following expressions for FWHM values of Gaussian Γ_G and Lorentzian Γ_L :

$$\Gamma_G^2 = \sigma_1^2 d^2 + \sigma_2^2 d^4 + \sigma_0^2 \quad (3.37)$$

$$\Gamma_L = \gamma_1 d + \gamma_2 d^2 + \gamma_0 \quad (3.38)$$

where the Γ_G and Γ_L are the Gaussian and Lorentzian FWHM, σ_0^2 and γ_0 are the contribution of Gaussian and Lorentzian components for instrument broadening, σ_1^2 and γ_1 are for Gaussian and Lorentzian strain broadening, and σ_2^2 and γ_2 are for Gaussian and Lorentzian size broadening, respectively.

The integral breadth, as a combination of Gaussian and Lorentzian components, was adopted as a more accurate measurement of peak width than the full width at half maximum (FWHM). As the parameters in Eq. 3.37 and Eq. 3.38 are the Gaussian and Lorentzian FWHM (Γ_G and Γ_L), they can be converted to the Lorentzian and Gaussian integral breadths (β_G and β_L), with then factors proposed in [170]:

$$\beta_L = \frac{\pi}{2} \Gamma_L \quad (3.39)$$

$$\beta_G = \frac{1}{2} \sqrt{\frac{\pi}{\ln 2}} \Gamma_G \quad (3.40)$$

Therefore, the total size integral breadth β_S and strain integral breadth β_D could be determined following equation below:

$$\beta_i = (\beta_G)_i \exp(-k^2) / [1 - \text{erf}(k)] \quad (3.41)$$

where i stands for size effect S and strain effect D ; k is a characteristic integral–breadth ratio of the size and strain broadened Voigt profile, $k = \beta_L / \pi^{1/2} \beta_G$.

Based on the good fitting of observed diffraction profile through least-squares fitting, after a series of convolution and deconvolution procedures on the Gaussian and Lorentzian components, the size integral breadth β_S and strain integral breadth β_D for each phase in studied materials were simultaneously obtained by Rietveld method in TOPAS program.

It is common practice to estimate crystallite size and microstrain values from peak broadening [171], which is respectively described by volume-weighted domain size D_V and the upper limit (maximum) of microstrain e . The volume-weighted domain size D_V and the upper limit (maximum) of microstrain e were determined respectively, with the following equations [169].

$$D_V = DIFC / \beta_S \quad (3.42)$$

$$e = \beta_D / 2DIFC \quad (3.43)$$

where $DIFC$ is the diffractometer constant, as mentioned in Eq. 3.19 and Eq. 3.20.

Chapter 4

Properties of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites

As stated in the objectives of this work (chapter 1), for the future development of laminate ceramics (design, manufacture and interpretation of properties), it is essential to firstly well understand the properties of monolithic materials using the combined layers with the same composition and obtained by the same processing method. In this chapter the monolithic $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials (A/Y-TZP), made by the novel tape casting green processing [93, 109] with tapes in the same composition, have been characterized and compared with the reference materials obtained by conventional slip casting method. Effect of addition of reinforcement Y-TZP on the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites was also studied.

A series of experimental data are presented: density, grain size, elastic modulus, hardness, flexure strength and fracture toughness, as well as the microstructure analysis. The properties of the materials can be the basis of the design and development of laminated ceramic materials in the future work.

4.1 Density and Microstructure

The A/Y-TZP samples data about density and average grain size are reported in **Table 4.1**. High densities (relative density > 98% T.D.) were achieved in all the studied A/Y-TZP materials. The density of A/Y-TZP composites was increased as the zirconia reinforcement content increased, due to the relatively higher density of Y-TZP (6.1 g/cm^3) than the one of $\alpha\text{-Al}_2\text{O}_3$ (3.99 g/cm^3). It indicates that the addition of zirconia particles allowed the densification of alumina matrix.

Table 4.1. Values of measured density (ρ), relative density (ρ_{relative}) and average grain size (G) in A/Y-TZP composites investigated.

	Y-TZP (vol. %)	Casting Techniques	ρ (g/cm^3)	ρ_{relative} (T.D. %)	G (μm)	
					G_A	$G_{\text{Y-TZP}}$
A-5YTZP (slip)	5	Slip casting	4.03 ± 0.06	98.4 ± 0.1	1.9 $\pm$ 0.3	0.3 $\pm$ 0.1
A-5YTZP (tape)	5	Tape casting	4.02 ± 0.06	98.2 ± 0.2		
A-40YTZP (slip)	40	Slip casting	4.77 ± 0.07	98.7 ± 0.2	1.0 $\pm$ 0.2	0.4 $\pm$ 0.2
A-40YTZP (tape)	40	Tape casting	4.76 ± 0.02	98.5 ± 0.1		

Characteristic microstructures of the studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites are shown in **Fig. 4.1**, as a function of Y-TZP reinforcement content. Very similar microstructures were exhibited by the slip casting and tape casting A/Y-TZP samples with the same composition. Thus the representative scanning electron micrographs of A-5YTZP and A-40YTZP composites were presented in **Fig. 4.1** (a) and (b), respectively, on the behaviour of both slip casting and tape casting samples. Dense microstructure was observed in all the studied materials, where the alumina matrix (in dark grey) and zirconia particulates (in light grey) were generally well-dispersed. The grain size of Al_2O_3 matrix was obviously decreased as zirconia content increased, as reported in **Table 4.1**. The inhibition effect of the second phase on matrix growth was manifested. Narrow grain size distributions were observed for both phases in each composite. It was clear that the fine and bimodal distribution of particle sizes allowed the most efficient fulfilling of the matrix for uniaxially pressing, promoting better densification of the powders [172].

In A-5YTZP composites (**Fig. 4.1 (a)**), the fine zirconia particulates were homogeneously distributed and located mainly at the triple points and grain boundaries of alumina matrix. In A-40YTZP composites (**Fig. 4.1 (b)**), with more addition of Y-TZP second phase, the interconnection between Y-TZP grains were apparently increased. Some of Y-TZP particles clustered together as submatrix, where alumina grains were separated and surrounded by Y-TZP particulates.

Fig. 4.1. SEM micrographs of polished and chemical etched surfaces of the studied materials: (a) A-5YTZP composites (both slip casting and tape casting samples). (b) A-40YTZP composites (both slip casting and tape casting samples). Al_2O_3 grains appear with dark grey color and Y-TZP particulates are in (bright) light grey color.

X-ray diffraction analysis of the studied samples in previous work (Fig. 4.2)[128] reported that only crystalline phases of α - Al_2O_3 and tetragonal Y_2O_3 -stabilized zirconia (Y-TZP) were found in both the sintered A-5YTZP and A-40YTZP composites. As mentioned in section 3.2, the raw zirconia powder include 30 vol.% monoclinic (*m*) zirconia phase and 70 vol.% tetragonal Y_2O_3 -stabilized zirconia (*t*). Therefore, it was demonstrated that during the manufacturing process, all the monoclinic zirconia phase was transferred into tetragonal zirconia, and furthermore, the tetragonal phase was fully retained in composites after sintering and cooling. This phase composition is desirable for obtaining materials with good mechanical properties.

Fig. 4.2. X-Ray diffraction profiles of the sintered $\text{Al}_2\text{O}_3/\text{Y-TZP}$ (tape casting) composites [128].
(a) A-5YTZP(tape); (b) A-40YTZP(tape)

All the above density, microstructure and phase composition analysis results seem not to depend on the particular casting technique, which indicates that the microstructure quality was not changed in ceramics fabricated by the novel tape casting method.

4.2 Elastic modulus

The elastic modulus was measured by both dynamic method (impulse excitation of vibration) and static method (three-point bending test).

During the dynamic test, the values of resonance frequencies collected showed very low variability in all cases, demonstrating absence of heterogeneities and appreciable porosity in the studied A/Y-TZP composites. The determined values of dynamic Young's modulus, shear modulus and Poisson's ratio by dynamic test were summarized in **Table 4.2**.

Table 4.2. The determined values of dynamic Young's modulus (E_{dyn}), shear modulus and Poisson's ratio (ν) by dynamic test and static Young's modulus (E_{flex}) by three-point bending test.

	E (GPa)		Poisson's ratio ν	Shear modulus (GPa)
	Static E_{flex}	Dynamic E_{dyn}		
A-5YTZP(slip)	102 ±20	372 ±1	0.25	155±1
A-5YTZP(tape)	110 ±30	375 ±4	0.25	156±1
A-40YTZP(slip)	78 ±18	301 ±4	0.28	121±1
A-40YTZP(tape)	80 ±16	303 ±4	0.28	121±1

The static Young's modulus, determined by three-point bending tests, was also presented in **Table 4.2** for comparison. **Fig. 4.3** shows the linear section of the stress-strain curves used for the calculation of the elastic modulus in three-point bending tests. It's clear that the slopes of stress-strain lines were obviously decreased as Y-TZP content increased in A/Y-TZP composites. With the same Y-TZP vol.%, the samples from the novel tape casting processing showed slightly higher slopes than the slip casting samples. The obtained values of static Young's modulus from three-point bending test, as well as its repeatability, are much lower than those from the

dynamic method. Such divergence was also reported by other researchers [173, 174]. In general, the values of elastic modulus of materials depend on the method used for determination [175, 176]. The dynamic method represents purely elastic behaviour without incorporating the effect of microcracks in the microstructure.

Ignoring this difference, decreasing trends of elastic modulus with the increase in Y-TZP content in A/Y-TZP composites were clearly exhibited in both dynamic and static tests. According to other published work [177], the results determined by dynamic method are more reliable. The following discussion was conducted based on the dynamic test results.

Fig. 4.3. The linear section of stress-strain curves for determination of the elastic modulus, obtained by means of three-point bending tests.

Comparing the results of the samples with the same Y-TZP content but manufactured by different green processing methods (the novel tape casting and conventional slip casting), the measured elastic modulus are very similar. Such similarity was consistent with the behaviors discussed before as to the microstructure equality and density of the materials obtained by the two methods. It is observed that the values of elastic modulus were decreased as Y-TZP content increases in A/Y-TZP composites, being in accordance with reports in [172, 178, 179]. The obtained E values were close to prediction by rule of mixtures starting from the values corresponding to a slip casting alumina material with 99% of theoretical density ($E = 400$ GPa, $\nu = 0.22$) and those corresponding to Y-TZP ($E = 210$ GPa, $\nu = 0.31$), demonstrated the high density and low defects number in materials.

4.3 The Vickers Hardness

The Vickers hardness of each studied A/Y-TZP was determined by Vickers indentation test, which was performed on the polished cross sections of samples under an indentation load of 100 N. For the tape casting samples, the cross section of tape-stacking surface was chosen for investigation, in order to obtain indentations at the interface areas and indentations in the centers of the constituent tapes. **Fig. 4.4** (a) shows the schema of the investigated cross sections with different positions of the indentation points.

Fig. 4.4. Scheme of the Vickers indentation at the polished cross section of the sintered A/Y-TZP samples. (a) Indentation performed in the interface zone (◇) and in the constituent tapes (◆). (b) scheme of top view of the indentation imprints and cracks formed.

The values of the Vickers hardness as well as the quantitative parameters of the Vickers indentation imprints (2a) and cracks (2c) are summarized in **Table 4.3**. It details a decreasing trend of hardness as Y-TZP content increases in A/Y-TZP composites, which was decreased from around 17.5 GPa to 15.2 GPa with the addition of Y-TZP increasing from 5 vol. % to 40 vol. %. Due to high density ($\rho_{\text{relative}} > 98\%$ T.D.) has been achieved for all samples studied (**Table 4.1**), the variation in porosity as increasing Y-TZP content did not bring about a great effect on the hardness of A/Y-TZP composites. The decrease in hardness obeys a linear mixture rule [110], considering the hardness of monophase materials of Al_2O_3 and Y-TZP, which was reported [180] as 18.3 GPa and 12.7 GPa, respectively. Similar hardness results were obtained in previous works in alumina–zirconia (Y_2O_3 -stabilized) ceramic system, with hardness varying between 12 and 18 GPa as the zirconia content decreased [181]. The Vickers hardness of ceramic materials is

generally affected by the intrinsic deformability of the ceramic and micro-structural features such as multiphases, grain size and orientation, porosity as well as boundary constitution [182]. The small standard deviation in each sample indicates the homogeneity of materials.

Table 4.3. Sizes of Vickers indentation cracks and imprints at the cross sections of sintered A/Y-TZP pieces, as well as the Vickers hardness H_V .

Samples	Indentation load, P (N)	Imprint Size, 2a (μm)	Crack Size, 2c (μm)	cracks-to-indent, c/a	Vickers hardness, H_V (GPa)
A-5YTZP (slip)	100	103 $\pm$ 2	332 $\pm$ 5	3.22	17.5 $\pm$ 0.2
A-5YTZP (tape)	100	103 $\pm$ 2	328 $\pm$ 5	3.17	17.5 $\pm$ 0.2
A-40YTZP (slip)	100	109 $\pm$ 2	272 $\pm$ 6	2.49	15.6 $\pm$ 0.2
A-40YTZP (tape)	100	110 $\pm$ 3	260 $\pm$ 5	2.36	15.3 $\pm$ 0.3

The typical top view of Vickers indentation imprints and cracks for each studied A/Y-TZP composites was presented in **Fig. 4.5**. Indentation cracks were observed in all samples, arisen from the corner of imprints. Remarkable similarity was observed between samples with the same Y-TZP content manufactured using different processing techniques (tape casting and slip casting).

Fig. 4.5. The typical top view of Vickers indentation imprints and cracks in A/Y-TZP composites. (a) A-5YTZP(slip); (b) A-5YTZP(tape); (c) A-40YTZP(slip); (c) A-40YTZP(tape)

Comparing the cracks formed in each indentation point, similar crack length was observed in the same diagonal line of the imprint (with $C1 \approx C1'$, $C2 \approx C2'$ in Fig. 4.4 (b)). The cracks formed in the two diagonal lines were also almost equal, with $2C1 = 2C2$, regardless of the tape casting samples and slip casting samples. The crack propagations from different corner were almost isotropic.

The sizes of indentation cracks and imprints were varied as a function of Y-TZP addition in composites (Table 4.3). As can be seen, with Y-TZP content increased from 5 vol.% to 40 vol.%, a slight increase in the size of indentation imprints (2a) was observed, whereas a significant decrease was exhibited in the indentation cracks (2c). It is highly related to the mechanical properties of materials, which will be discussed in the following sections.

No significant difference was observed between the values in different measured positions on the same sample, according to the standard deviation values. It confirms the microstructure uniformity and strong interfaces between different tapes.

4.4 Flexure Strength

After three-point bending test, the average values of flexure strength, σ_f , were determined, as summarized in Table 4.4. The apparent stress-strain curves were presented in Fig. 4.6. The relatively large standard deviation of flexure strength in each material can be understood, because the ceramic strength values usually exhibit a large scattering (up to 100%) even for high performance ceramics [183].

Table 4.4. The average values of flexure strength, σ_f , determined by three-point bending test.

Materials	σ_f (MPa)
A-5YTZP(slip)	380 $\pm$ 40
A-5YTZP(tape)	390 $\pm$ 30
A-40YTZP(slip)	510 $\pm$ 30
A-40YTZP(tape)	520 $\pm$ 50

Fig. 4.6. Experimental apparent stress–strain curves in three-point bending test on the investigated $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites.

The value of the flexural strength increased with the Y-TZP vol.% in A/Y-TZP composites was exhibited. The average value of flexure strength in A-5YTZP composites is about 385 MPa, and that in A-40YTZP composites is about 510 MPa. Comparing with the pure alumina ceramics manufactured by slip casting ($\sigma_f=300$ MPa) [49], it presented more than 28 % and 70 % of flexural strength in A-5YTZP composites and A-40YTZP composites, respectively. The increase of flexure strength tends to indicate the materials with a more dense and refined microstructure, as well as a reduced size of the crack population. The strength of ceramics was reported [184] to be inversely proportional to the square root of the grain size. As described in section 4.1, in present work, with the increase of Y-TZP content in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites, the microstructure characterization showed a decrease in

grain size of Al_2O_3 matrix and a slight increase in density. The increase of flexure strength in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites corresponds well with the microstructure characterization, as a function of Y-TZP second phase addition.

4.5 Fracture toughness assessment

As described in section 3.3.3.4, the model I fracture toughness (K_{Ic}) of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites was evaluated by two different methods: (i) the Single Edge Laser-Notch Beam (SELNB) method [134-136] and (ii) the indentation fracture (IF) method [137, 138]. The fracture toughness studies in both methods were analyzed in detail in the following sections.

4.5.1 The Single Edge Laser-Notch Beam method (SELNB)

4.5.1.1 Fracture toughness K_{Ic}

The Single Edge Laser-Notch Beam (SELNB) method, conducted using the three-point bending test on sample bars with ultra-sharp V notch by laser assisted-machining, was used for fracture toughness determination. The laser notch was produced with a consistent geometry, with a relative notch depth, $\alpha=a/W\approx 0.05$.

Fig. 4.7. Representative load-displacement curve recorded during the single edge laser-notch beam (SELNB) bending tests.

The characteristic load-displacement curves of the bending tests for the studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials with laser notch were shown in **Fig. 4.7**. As can be seen, typical brittle fracture was exhibited in all samples, which is consistent with the linear elastic behavior before reaching the maximum load value.

The fracture toughness K_{IC} values were calculated using Eq.3.9, with the values summarized in **Table 4.5**. It was found that as Y-TZP content increased from 5 vol. % to 40 vol. %, the fracture toughness of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites was increased from the range of $4.2\sim 4.6 \text{ MPa}\cdot\text{m}^{1/2}$ to $5.4\sim 6 \text{ MPa}\cdot\text{m}^{1/2}$. This increasing trend agreed well with the work reported in the literature [172, 179]. A slight improvement in K_{IC} can be seen in tape casting samples when compared to slip casting samples with the same Y-TZP content.

Table 4.5. The fracture toughness K_{IC} of the studied A/Y-TZP composites obtained by Single Edge Laser-Notch Beam (SELNB) method.

Materials	SELNB $K_{IC} (\text{MPa}\cdot\text{m}^{1/2})$ ($a/w\approx 0.05$)
A-5YTZP(slip)	4.2 ± 0.2
A-5YTZP(tape)	4.6 ± 0.3
A-40YTZP(slip)	5.4 ± 0.8
A-40YTZP(tape)	6.0 ± 0.4

The determined K_{IC} values in this study using SELNB method are acceptable, compared with those reported in literature for similar compositions and determined by other conventional methods such as single edge notch bending test (SENB) [50, 185] or bending of the specimens with Vickers indentations [185, 186]. For example, Tuan *et al.* [50] obtained fracture toughness values of $\sim 5.0 \text{ MPa}\cdot\text{m}^{1/2}$ for A-5YTZP materials with similar microstructure. While in [48], the K_{IC} value was reported as $\sim 4.0 \text{ MPa}\cdot\text{m}^{1/2}$ for alumina-zirconia composites with 5 vol. % zirconia reinforcement.

Taking monophase alumina as reference materials, which presents an entirely brittle behavior [187], the K_{IC} value of alumina with similar grain sizes was reported as $K_{IC} \sim 3.5\sim 4.5 \text{ MPa}\cdot\text{m}^{1/2}$, determined from various tests [143, 188]. With a comparison between K_{IC} values of monophase alumina and $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites in present work, it is clear that the mechanical properties of $\text{Al}_2\text{O}_3/\text{Y-}$

TZP composites were improved with the addition of Y-TZP second phase. It was proposed that [185] the R curve behavior can be activated by the presence of Y-TZP as a second phase in alumina-based ceramics.

The increase in fracture toughness in A/Y-TZP composites could be attributed to the $t\text{-ZrO}_2 \rightarrow m\text{-ZrO}_2$ phase transformation [189], microcrack formation [190, 191], as well as the internal residual stresses [192, 193] in composites. Detailed toughening mechanism of the studied A/Y-TZP composites was discussed combining with the fractographic observation.

4.5.1.2 Fractographic Observation

The fracture surfaces of studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials after SELNB test were firstly observed at low magnification, shown in **Fig. 4.8**. The laser pre-notch was at the bottom of the view of fracture surface in **Fig. 4.8**. As a comparison, the specimen manufactured using the novel tape casting techniques shows a relatively more tortuous fracture surface, comparing with the slip casting samples with the same compositions. At a low magnification, part of interface between tapes was revealed on the fracture surface of tape casting samples. For all the studied A/Y-TZP composites, the fracture surfaces showed a transformation from the rough initial fracture part (close to pre-notch, at the bottom part of the view in **Fig. 4.8**) to a relatively flat appearance at the later fracture part (the top part of the view in **Fig. 4.8**, far from the pre-notch of samples). The fracture surfaces of tape casting samples are rougher than those in slip casting samples, which might indicate a higher fracture resistance.

Fig. 4.8. The fracture surfaces of studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials at low magnification.
 (a) A-5YTZP(slip); (b) A-5YTZP(tape); (c) A-40YTZP(slip); (d) A-40YTZP(tape)

The fracture part near the notch edge, as the initial fracture areas, was carefully investigated by scanning electron microscope. No obvious regular semi-elliptical surface cracks were observed in this area in all samples. The representative view of this fracture region was shown in **Fig. 4.9**. It showed three well-differentiated regions: the flat region A, corresponds to pre-notch part machined by laser techniques; the next region B, extends generally around $30\sim 40\mu\text{m}$ between notch and fracture region; and region C is the usual common fracture section. Higher amplification of region B (**Fig. 4.9** (b)) shows small and regular slits patterns which are generally parallel to the fracture direction during bending test. These slits patterns were mainly introduced by the machining process on region B. As marked by arrows in **Fig. 4.9** (b), the fracture origins were mainly from the tips of slits in region B and then extend to the part C.

Fig. 4.9. The represent view of fracture part near the notch edge in A-40YTZP (tape) composites, without regular semi-elliptical surface cracks. (a) the whole view, including three well-differentiated regions: flat region A (pre-notch part), region B (with small and regular slits patterns), and region C (the usual common fracture part). (b) Detail view of region B with higher amplification.

A detailed characterization of fracture surface was observed at high magnification by SEM, as shown in **Fig. 4.10**. Due to very similar fracture features shown by slip casting and tape casting A/Y-TZP samples with the same Y-TZP content, hereby the representative fracture morphologies of A-5YTZP and A-40YTZP composites were presented in **Fig. 4.10** (a)&(b) and (c)&(d) (for both slip casting and tape casting samples). It was observed that all the studied materials were dense and homogeneously made up of two phases: $\alpha\text{-Al}_2\text{O}_3$ matrix (dark grey) and Y-TZP second phase (light grey), with roughly uniform grain size and regular grain shape for each phase. Several “cleavage fractures” were observed in the transgranular fracture surface of Al_2O_3 grains in all tested A/Y-TZP samples, which implied a strong interface between the particle and matrix.

Irrespective of the manufacturing methods, the fracture features of A/Y-TZP samples were different as a function of Y-TZP content. The grain size of Al_2O_3 matrix was obviously reduced as Y-TZP content increased, as well as an increase in Y-TZP grain size itself. Such inhibition effect of the second phase on growth of matrix was discovered in previous works [194-196], and related to theories of grain growth kinetics in a two-phase solid. It was beneficial for the reinforcement of microstructure and also the mechanical properties [51].

Fig. 4.10. Scanning electron micrographs of the fracture surfaces of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites: α - Al_2O_3 matrix, in dark grey color; second phase Y-TZP, in light grey color; microcracks were indicated by the arrows.

(a) the representative fracture morphology of A-5YTZP composites (both slip casting and tape casting samples, due to the very similar fracture features between them); (b) Detail of microcracks in A-5YTZP composites;

(c) the representative fracture morphology of A-40YTZP composites (both slip casting and tape casting samples); (d) Detail of microcracks in A-40YTZP composites.

In A-5YTZP composites (**Fig. 4.10** (a) and (b)), Y-TZP particulates were homogeneously distributed and mainly located at the triple points and grain boundaries of alumina matrix. Both of intergranular and transgranular fracture modes were observed in A-5YTZP samples, with transgranular fracture being mainly observed in some larger alumina grains. The main contribution to fracture energy was assumed to come from the alumina matrix.

With the increasing addition of Y-TZP in A-40YTZP composites (**Fig. 4.10** (c) and (d)), Y-TZP grains were apparently more interconnected, whereas alumina grains became more isolated and surrounded by Y-TZP grains. The fracture modes still remained as mixed inter/transgranular fractures. However, the predominant transgranular fracture in composites occurred in Y-TZP particles instead of Al_2O_3 matrix, with almost all of Y-TZP grains showing a transgranular fracture. In this case, most of fracture energy was absorbed by Y-TZP particulates, leading to Al_2O_3 matrix being protected. The fracture mode in Al_2O_3 matrix was mainly intergranular fracture, with transgranular fracture only in a few large Al_2O_3 grains.

The toughness increase as addition of Y-TZP second phase in alumina-zirconia composites is mostly expected to be attributed to the tetragonal-to-

monoclinic (martensitic) phase transformation in zirconia, that has been extensively studied [111, 112, 189, 197-200]. The phase transformation, which is accompanied by volume expansion (4-5%) and shear strain (1-7%), will provide a compressive stress which acts to reduce and eventually stop the propagation of the crack, which needs extra work for further crack propagation and fracture. As analyzed by X-ray diffraction for the studied samples (**Fig. 4.2**), the tetragonal zirconia phase in composites was fully retained after sintering in present work. Therefore, with more addition of Y-TZP in composites, there was more amount of tetragonal phase available for $t \rightarrow m$ phase transformation during fracture, which caused the improvement in fracture toughness.

Microcracks were observed on the fracture surfaces of both A-5YTZP and A-40YTZP samples, where those in the latter were more significant than those in the former. As indicated by the arrows in **Fig. 4.10** (a) and (b), a few of microcracks were formed around the embedded Y-TZP grains and along grain boundaries between alumina and Y-TZP particulates during the fracture process in A-5YTZP composites. As Y-TZP content increased to 40 vol.%, more microcracks were observed on the fracture surface, which were not only along grain boundaries of Al_2O_3 and Y-TZP, but also traversed Y-TZP grains, as shown by the arrows in **Fig. 4.10** (c) and (d). It could be explained by considering that as external stresses was imposed and crack propagated in composites, the transformation of $t\text{-ZrO}_2 \rightarrow m\text{-ZrO}_2$ was activated, followed by the occurrence of the ZrO_2 grain cracking and microcracks nearby the main crack, due to the volume expansion of ZrO_2 . These microcracks could lead to the branching of the main crack and then increase fracture surface, contributing to the increase of the total energy consumed during crack propagation. Stress concentration at the main crack tip would then be relaxed and the driving force of the main crack would be reduced accordingly.

It was demonstrated that the stress-induced phase transformation toughening and transformation-induced microcrack toughening mechanisms were responsible for the improved fracture toughness of A/Y-TZP composites. Other possible mechanisms which enhance the fracture properties, e.g. crack deflection [201], was hardly to be judged only by fractographic observation. A complementary study was carried in the following indentation fracture method. And the effect of residual stresses on mechanical properties of A/Y-TZP composites will be specially investigated in detail in Chapter 5.

4.5.2 The indentation fracture (IF) method

4.5.2.1 Crack system model and K_{IC} calculation

The indentation fracture (IF) method was used for determining the fracture toughness of Al₂O₃/Y-TZP ceramics, with an applied load of 100 N on the Vickers indentation test. The value of K_{IC} was determined by direct crack measurement and calculation with different equations, as summarized in **Table 4.6**.

Table 4.6. The fracture toughness K_{IC} of the studied A/Y-TZP composites obtained by the indentation fracture (IF) method using different equations.

Materials	cracks-to-indent c/a	Indentation K_{IC} (MPa·m ^{1/2})			
		Median cracks $c/a > 2.5$		Palmqvist Cracks $c/a < 2.5$	
		Anstis <i>et al.</i> [138]	Laugie <i>et al.</i> [148]	Shetty <i>et al.</i> [147]	Niihara <i>et al.</i> [146]
A-5YTZP (slip)	3.22	3.4±0.2	3.5±0.2	5.8±0.2	7.5±0.2
A-5YTZP (tape)	3.17	3.6±0.4	3.7±0.4	5.9±0.3	7.7±0.2
A-40YTZP (slip)	2.49	4.3±0.2	4.3±0.2	6.5±0.2	8.1±0.2
A-40YTZP (tape)	2.36	4.6±0.2	4.7±0.2	6.7±0.3	8.4±0.2

Several equations are available for calculation of fracture toughness in the IF methods. As can be seen in **Table 4.6**, using different calculation equations, remarkable differences in fracture toughness values were found for the same material. In order to get reliable and comparable fracture toughness values through the IF method, the selection of a proper equation is crucial, which depends highly on the identification of the type of cracks formed. As previously described in section 3.3.3.4, the crack model was determined by two methods in present work: (i) the empirical way according to the ratio of cracks-to-indent size (c/a) at indented sample surface, where a is the half-diameter of the indentation imprint, and c is crack length measured from the center of indent to the crack tip, and (ii) the observation methods on the top sample surfaces, which has been sequentially polished down to some depth after Vickers indentation (**Fig. 3.6**).

According to the ratio of cracks-to-indent size (c/a) and empirical rule [149], there were two types of crack models obtained in Vickers indentation test, where A-

5YTZP composites presented half-penny cracks with $c/a > 2.5$, and A-40YTZP composites behaved like Palmqvist cracks model with smaller ratio of $c/a < 2.5$. With the same Y-TZP addition in A/Y-TZP composites, similar ratio of c/a was obtained both in the tape casting samples and slip casting samples. It seems that the difference in the manufacturing processing investigated (the novel tape casting and conventional slip casting) did not obviously affect the crack models.

Considering the complication of crack behavior and potential uncertainty brought about by empirical methods, it is usually insufficient to identify the crack model by using only a single method. Therefore, the observation method was used as a complement to crack model identification. The characteristic top views of Vickers indentation imprint and crack, as well as the views of sequentially polished surface up to a certain depth (e.g. the depth of h_1 and h_2 in **Fig. 3.6**), were presented in **Fig 4.11** (A-5YTZP composites) and **Fig. 4.12** (A-40YTZP composites). The evolution of indented surface view was clearly visible, and this way the type of crack could be determined.

Fig. 4.11. The evolution of indented surface view in A-5YTZP composites (for both tape casting and slip casting samples). (a) the original top views of Vickers indentation imprint and crack of A-5YTZP; (b) the view of indented surface which was sequentially polished down to the depth of h_1 in **Fig. 3.6** after indentation; (c) the view of indented surface which was sequentially polished down to the depth of h_2 in **Fig. 3.6** after indentation.

For A-5YTZP composites (**Fig. 4.11** a, b and c), at the first period of polishing (e.g. the represented depth of h1), cracks were always connected with the corner of indentation imprints (**Fig. 4.11** b). Once the polished depth was enough (e.g. the depth of h2 in **Fig. 3.6**) so that the imprint was almost removed, the connected crack still existed (**Fig. 4.11** c). A typical model of median/half-penny cracks was determined in A-5YTZP composites. However, the indentation crack geometry observed in A-40YTZP composites (**Fig. 4.12** a, b and c) was much different from the one in A-5YTZP. Disconnected radial cracks, as shown in **Fig. 4.12** b and c, were observed in sequentially polished top surfaces of A-40YTZP specimen, which is in agreement with the Palmqvist crack geometry. The observation of indentation cracks in both A-5YTZP and A-40YTZP composites agreed well with Baudin *et al.*'s research work [202], which suggests that the shape of the indentation cracks changes with the amount of second phase in alumina-3YTZP composites.

Fig. 4.12. The evolution of indented surface view in A-40YTZP composites (for both tape casting and slip casting samples). (a) the original top views of Vickers indentation imprint and crack of A-40YTZP; (b) the view of indented surface which was sequentially polished down to the depth of h1 in **Fig. 3.6** after indentation; (c) the view of indented surface which was sequentially polished down to the depth of h2 in **Fig. 3.6** after indentation.

According to the above, it could be determined that A-5YTZP composites presented half-penny cracks, whereas the cracks in A-40YTZP composites behaved

according to Palmqvist model. The indentation K_{Ic} values of A-5YTZP composites were therefore calculated by half-penny crack model equations (in **Table 3.2**)—Anstis and Laugier's equations, and those of A-40YTZP composites were calculated by corresponding Palmqvist crack equations—Shetty and Niihara's equations. As shown in **Table 4.6**, the fracture toughness K_{Ic} of A/Y-TZP composites was mainly affected by the addition of Y-TZP second phase. Irrespective of the manufacturing methods, the indentation K_{Ic} showed a consistent range of 3.4~3.7 MPa·m^{1/2} in A-5YTZP composites, and those in A-40YTZP composites were determined as 6.5~6.7 MPa·m^{1/2} and 8.1~8.4 MPa·m^{1/2} respectively, corresponding to Shetty and Niihara equations. The obtained K_{Ic} values of A-5YTZP composites are slightly lower than that reported in Moraes *et al.*'s work ($K_{Ic} = 4.25 \pm 0.06$ MPa·m^{1/2}) [172], which was using the same indentation condition and calculated by Anstis's equations. This difference might due to the different density of materials, where higher density ($\rho_{\text{relative}} \approx 99.29\%$) was obtained in Moraes *et al.*'s work, compared with those in this work ($\rho_{\text{relative}} \approx 98.4\%$).

As regards the A-40YTZP composites, the difference between K_{Ic} results from Shetty and Niihara equations was approximately 25%. This K_{Ic} difference with different equations was also argued by other researchers [203, 204]. According to the SELNB results in **Table 4.5**, K_{Ic} results estimated from Shetty *et al.*'s equation seems more reliable for A-40YTZP composites in present work, with the values of 6.5~6.7 MPa·m^{1/2}.

Regardless of the calculation equation employed, with the same Y-TZP addition, the differences between K_{Ic} of the novel tape casting samples and of slip casting samples are not remarkable. Only a slight improvement in fracture toughness was observed in the tape casting samples, compared with the slip casting reference samples and using the same calculation equations.

According to the above, using indentation fracture (IF) method, the relatively reasonable and reliable results of fracture toughness were summarized with K_{Ic} value of A-5YTZP composites being around 3.4~3.7 MPa·m^{1/2}, and the one of A-40YTZP composites being 6.5~6.7 MPa·m^{1/2}.

4.5.2.2 Indentation crack propagation paths

As particulate-reinforced composites, it is hard to say whether the grains have acted as strong ligaments by observing the fracture surfaces after the bending test. In order to figure out the fracture mechanism in more detail as well as to better understand

the toughening mechanism, observations of the interaction between the crack path and microstructure were made on the extended cracks of Vickers indentation. Very similar indentation crack behavior was observed in tape casting and slip casting samples with the same Y-TZP addition. SEM micrographs of typical indentation crack profiles in A-5YTZP and A-40YTZP composites were illustrated in **Fig. 4.13** and **Fig. 4.14**, respectively, irrespective of the manufacturing techniques.

Fig. 4.13. Typical indentation crack profiles in A-5YTZP composites, representing both tape casting and slip casting samples.

Fig. 4.14. Typical indentation crack profiles in A-40YTZP composites, representing both tape casting and slip casting samples.

A mixed transgranular and intergranular fracture modes were revealed in both A-5YTZP and A-40YTZP composites, as shown in **Fig. 4.13 (a)** and **Fig. 4.14 (a)**, where red arrows marks the occurrence of transgranular fracture and black arrows indicates intergranular fracture. Differences can be seen between the fracture modes of A/Y-TZP composites, as a function of Y-TZP addition. In A-5YTZP composites (**Fig. 4.13**), the predominant fracture mode is the intergranular fracture. While in A-40YTZP composites (**Fig. 4.14**), transgranular fracture of Y-TZP particles was the dominant failure mechanism. These behaviors agreed well with the fractographic observation of fracture surface after SELNB test (**Fig. 4.10**).

Crack deflection was observed in both the A-5YTZP and A-40YTZP indented samples, where the main cracks were attracted toward the Y-TZP particles and then propagated along the interface between Al_2O_3 matrix and Y-TZP particles for some distance. The amount of crack deflection appeared to increase with increasing Y-TZP particle content. This crack deflection in microstructures of a wide variety of phase-transformation-toughened ceramics were also reported by Faber and Evans [113]. It could be a contributing factor to the toughness enhancement of the ZTA composites.

In addition, crack bridging and crack branching was observed in A-40YTZP composites, which mainly occurred in Y-TZP particles, as shown in **Fig. 4.14**.

These phenomena are usually associated with the following aspects:

- 1) Stress-induced phase transformation and transformation-induced microcrack: As the indentation load is imposed and crack propagation is started, the $t \rightarrow m$ transformation in zirconia is activated. The associated volume expansion and shear strain could lead to ZrO_2 grain cracking and microcracks near the main crack. These microcracks contributed to the crack branching and then increase fracture surface, contributing to the increase of the total energy consumed during crack propagation. With more addition of Y-TZP in A-40YTZP composites, the interaction between the main cracks and Y-TZP second phase was increased, promoting microcrack generation. More cracks might cut through Y-TZP particulates, leading to the broken-out Y-TZP grains acting as crack bridging, as observed in **Fig. 4.14**.
- 2) The internal residual stresses: residual stresses were considered to exist in particle-reinforced composites, due to thermal and elastic mismatches between matrix and particulates [193, 202, 205]. The complex residual stresses state, in different scales (e.g. macro- and micro-), could also affect the crack profiles and mechanical performance. Detailed investigation into residual stresses distribution in the studied A/Y-TZP composites will be conducted in Chapter 5, as well as the effect on the mechanical and fracture behaviors.

4.5.3 Comparison between SELNB and IF

As can be seen from the above studies in sections 4.5.1 and 4.5.2, regardless of the methods used for K_{Ic} determination, the K_{Ic} results obtained by SELNB method (**Table 4.5**) and IF method (**Table 4.6**) showed similar trends as a function of Y-TZP

second phase addition and the manufacturing processing for studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites. Obvious increase of fracture toughness was observed with the increase of Y-TZP content, consistent with the works of [172, 206, 207]. Comparing A/Y-TZP materials with the same Y-TZP vol.%, samples manufactured using the novel tape casting technique showed relatively higher fracture toughness than those of slip casting samples, demonstrating the beneficial effect of the novel processing on mechanical properties in A/Y-TZP ceramics.

When comparing the K_{Ic} values obtained by means of SELNB method and IF method, some divergence was observed. For the studied A-5YTZP samples, the K_{Ic} from SELNB method is relatively higher than the determined Vickers indentation (IF) K_{Ic} . But in A-40YTZP composites, the K_{Ic} from SELNB test showed lower results comparing with the ones from IF method. This divergence was also discovered by [139, 208]. It could be understood that the use of several techniques to measure fracture toughness would yield different results possibly due to difference of crack mechanisms induced or triggered [209]. The SELNB method highly depends on the width and depth of the notch machined in the bending bars [139]. And for IF method, apart from the influence of sample surface condition, K_{Ic} measurement is directly related to precise determination of the exact crack length which is usually underestimated and results in increased fracture toughness values. The consistent estimation of K_{Ic} (IF) in each sample, according to the small values of standard deviation in **Table 4.5**, reflected the good quality of sample surface during the indentation test.

4.6 Nanoindentation measurement

Nanoindentation tests were carried out as an additional measurement of the hardness and the Young's modulus of the studied A/Y-TZP ceramics. A typical SEM micrograph of 1500 nm penetration depth imprint on materials is shown in **Fig. 4.15**. As can be observed, these indentations are large enough to include a representative portion of the microstructure and, consequently, to test the behavior of the composite.

Fig. 4.15. The typical SEM micrographs of 1500 nm penetration depth nanoindentation imprint on A-5YTZP(tape) materials.

Fig. 4.16. The representative indentation load (P)-displacement (h) curves of each A/Y-TZP composites.

Fig. 4.16 shows the representative indentation load (P)-displacement (h) curves of each A/Y-TZP composite obtained in this work. In all cases, P–h curves do not exhibit any sign of discontinuities or pop-in, indicating that fracture-like phenomena are not taking place during loading/unloading stages. It indicated that mechanical integrity of all the materials studied is retained throughout the indentation tests; and thus, the experimentally attained data and the subsequently extracted parameters can be accepted as reliable values for assessing the small-scale mechanical properties of the materials. An evident distinction between the indentation responses of A/Y-TZP as a function of Y-TZP addition can be deduced from the P-h curves. A slight difference was observed between the P-h curves of the tape casting samples and the

slip casting samples with the same Y-TZP addition in the A/Y-TZP composites, which are more obvious in materials with 5 vol.% of Y-TZP than those with 40 vol.% of Y-TZP.

Fig. 4.17. The elastic modulus (E) vs displacement (h) curves for all the A/Y-TZP materials investigated.

Fig. 4.18. Hardness (H) vs displacement (h) curves for all the A/Y-TZP materials investigated.

The evolution on the elastic modulus (E) and hardness (H) as a function of the penetration depth (h) for the materials studied are presented in **Fig. 4.17** and **Fig. 4.18**, respectively. It can be seen that the E and H results in the curve corresponding to the initial 300 nm of penetration depth are rapidly changing and unstable, possibly as a result of the implicit experimental variability of factors such as tip-sample interactions, sample roughness, and specially tip rounding. A description of the influence of indenter tip geometry on elastic deformation during indentation has been reported in the literature [210]. Therefore, the E and H values determined in this initial penetration depth regime are not taken into account for further analysis. As the indenter tip gets deeper, the extracted values for E and H become almost independent of the penetration depth in the all A/Y-TZP composites studied. Under these conditions, the average values of E and H for each sample can be assessed. The average values for the elastic modulus (E) and hardness (H) of the samples tested obtained using the continuous stiffness measurement (CSM) module from 25 indentations in each sample are listed in **Table 4.7**.

Clear differences in the E and H values were found as a function of the addition of Y-TZP in A/Y-TZP composites. As the Y-TZP vol.% increases, both the determined E and H values obviously decreased. These trends are in good agreement with the previous results obtained from large scale testing (e.g. static and dynamic elastic modulus measurement in section 4.2 and Vickers hardness in section 4.3). As a comparison, the nanoindentation tests gave a somewhat higher value of E and H for each sample than those obtained from large scale testing. For instance, the determined dynamic elastic modulus E for A-5YTZP and A-40YTZP composites are around 375 GPa and 303 GPa, respectively, whereas those by nanoindentation are 407~424 GPa and 340~346 GPa. As regards the hardness, the determined Vickers microhardness for A-5YTZP and A-40YTZP composites are around 17.5 GPa and 15.5 GPa, respectively, but those from nanoindentation are around 23.2~25.8 GPa and 22.6~22.8 GPa. Similar variations were also reported by other authors [211, 212]. It can be understood by considering the much smaller size of indenters and contact depth during nanoindentation (usually $<2\mu\text{m}$) when compared to the conventional large scale testing, for example, the contact depth during microindentation is typically 10–100 μm . The nanoindentation technique is more representative of the local characteristics of materials at the microstructural length scale, without much influence of defects in bulk scale, e.g. porosity, microcracks, etc. However, the conventional large scale testing, e.g. three-point bending, resonance technique, Vickers indentation, etc., would be affected by the overall defects and it would reflect the bulk characteristics of the test materials.

Taking the results from other researchers performing nanoindentation on alumina and zirconia, the E and H values of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites can be estimated by rule of mixtures. For example, Twigg *et al.* [213] used a Berkovich indenter producing results on $\alpha\text{-Al}_2\text{O}_3$ of ~ 24.7 GPa for hardness and 458 GPa for elastic modulus. W. G. Mao *et al.* [214] found that nano-hardnesses and an elastic modulus for polycrystalline $\alpha\text{-Al}_2\text{O}_3$ are about 30 ± 3 GPa and 466 ± 20 GPa, respectively. The reported results [213-217] for polycrystalline alumina were ranged in: hardness 20~35 GPa and elastic modulus 380~500 GPa. Yttria-stabilized zirconia (tetragonal) was measured by Y. Gaillard *et al.* [218] as 17.5 GPa for the hardness and 250 GPa for the elastic modulus. The evaluation for A-5YTZP composites (with 5 vol.% Y-TZP) can be approximated respectively as 373~487 GPa of E and 20~34 GPa of H , and for A-40YTZP composites (with 40 vol.% Y-TZP) it was estimated as 328~400 GPa for E and 19~28 GPa for H . It can be seen that our nanoindentation measurements results agree with the estimations made by rule of mixtures.

Table 4.7. The average elastic modulus (E) and hardness (H) of A/Y-TZP composites obtained by nanoindentation.

Materials	E (GPa)	H (GPa)
A-5YTZP(slip)	410 ± 20	23 ± 2
A-5YTZP(tape)	424 ± 10	26 ± 1
A-40YTZP(slip)	340 ± 8	22.6 ± 0.8
A-40YTZP(tape)	346 ± 7	22.8 ± 0.7

With the same Y-TZP content in A/Y-TZP composites, differences in the nanindentation determined elastic modulus (E) and hardness (H) between the novel tape casting samples and slip casting samples were detected. As shown in **Table 4.7**, the tape casting samples showed higher E and H than the conventional slip casting samples, especially in the composites with 5 vol.% Y-TZP reinforcement. A small scattering of the results obtained from different indentations in each sample was found for all tape casting samples.

4.7 Summary and Conclusions

Monolithic $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials, manufactured using the novel tape casting method [93, 109], were studied and compared with the materials produced by conventional slip casting, in terms of density, microstructure, mechanical and fracture properties (elastic modulus, hardness, flexure strength and fracture toughness). The effects of the addition of Y-TZP particles were investigated.

The main properties determined for the monolithic $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites with different zirconia contents (5 vol.% and 40 vol.%) and green processing routes (the novel tape casting and conventional slip casting) are summarized in **Table 4.8**. The following conclusions can be drawn:

- 1) The microstructures of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites obtained by the novel tape casting method are desirable, with high density (relative density $>98\%$ T.D.), defect-free interface between individual tapes, homogeneous dispersion of particles, as well as a narrow grain size distribution for both particles and matrix.
- 2) The tetragonal to monoclinic transformation of zirconia was controlled in the studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites during the sintering process, leading to an almost full retention of tetragonal zirconia phase in composites after manufacture.
- 3) Grain size and the microstructure of the materials changed with the Y-TZP volume fraction in composites. The grain size of Al_2O_3 matrix was reduced and the grain size of Y-TZP was slightly increased when the volume fraction Y-TZP was increased.
- 4) The materials density, flexural strength and fracture toughness were improved through the increase in the addition of Y-TZP particulates in A/Y-TZP ceramics. The Vickers hardness and elastic modulus were decreased.
- 5) Crack deflection, intergranular and transgranular fracture modes were observed in all fractured A/Y-TZP samples. As the Y-TZP content increased, the predominant fracture mode in the composites varied from intergranular to transgranular. With a higher Y-TZP content, crack branching and crack bridging was observed, mainly in the Y-TZP particles. It demonstrated that the stress-induced transformation toughening, and transformation-induced microcrack toughening mechanisms were responsible for the improved

mechanical properties in A/Y-TZP composites, and also maybe the internal residual stresses.

- 6) No significant effects were induced by the differential manufacturing processes (the novel tape casting and conventional slip casting), in terms of microstructure and mechanical performance of the A/Y-TZP ceramics studied. This ensures that the quality of ceramics manufactured by the novel tape casting method was sound (e.g. defect-free interface between individual tapes, homogeneities in microstructure, high mechanical performance, etc.), indicating the novel tape casting process could be a promising candidate for the manufacture of laminated ceramics in the future.

Chapter 5

Residual Stresses Analysis of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites

As introduced in chapter 3, residual stresses (RS) states in the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites studied were evaluated in macro- and micro- scales by constant-wavelength (CW) neutron diffraction and time-of-flight (TOF) neutron diffraction techniques. Through-thickness residual stress profiles of the alumina matrix and the zirconia particulates were obtained for all $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites studied, with the uniform and non-uniform residual stresses being detected. The RS results obtained were compared to data available in the literature and to existing theoretical models for particulate composites. Multi-phase qualitative and quantitative analyses, as well as crystal structure determination were achieved by Rietveld refinement. Microstructural information (domain size and crystal microstrain) was accessed by peak broadening analysis. The mechanical behavior of A/Y-TZP ceramics was further understood by combining the RS results and the mechanical properties (in Chapter 4). The interactions of microstructure, mechanical performance and residual stresses were discussed. The effects of the addition of second phase Y-TZP and green processing (the novel tape casting and conventional slip casting) were

discussed together with RS, crystallite structures, microstructure information and mechanical behavior. The properties of the materials could be the basis of the design and development of laminated ceramic materials in the future work.

5.1 Constant-wavelength neutron diffraction

Residual stress measurements were made by means of constant-wavelength (CW) neutron diffraction on the strain imager SALSA, in ILL. The through-thickness strain scanning was carried out for the individual phase in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites: Al_2O_3 and Y-TZP phase. Individual reflections of each phase, which were close to the Bragg angle of $2\theta \approx 90^\circ$, were selected for investigation. The detected peaks in this work are Al_2O_3 (300) and Al_2O_3 (116) for Al_2O_3 phase and YTZP (211) and YTZP (103) for Y-TZP phase. The detailed diffraction fitting and residual stresses analysis were given out at below.

5.1.1 Diffraction profiles analysis

The diffraction profiles of CW neutron were analyzed by LAMP software. Using the pseudo-Voigt model, the diffraction patterns were fitted and information on the peaks (peak position, intensity and FWHM, etc.) was extracted.

In order to obtain the stress-free lattice spacing, the Al_2O_3 starting powder was scanned and its diffraction patterns of Al_2O_3 (116) and Al_2O_3 (300) were carefully fitted. The measured diffraction profiles were presented in scatter plots and the fitting ones were in blue solid lines, as shown in **Fig. 5.1**. It shows that the detected peak Al_2O_3 (116) at $2\theta = 79.9^\circ$ was relatively narrower than the Al_2O_3 (300) at $2\theta = 96.8^\circ$. For Y-TZP starting powder, the measured and fitted diffraction patterns of YTZP (211) was given in **Fig. 5.2**, as well as a neighboring peak YTZP (103). Even though the two peaks are very close to each other and the peaks are rather noisy, by means of fitting in LAMP, the peak separation and identification was successfully achieved, with YTZP (211) at $2\theta = 83.8^\circ$ and YTZP (103) at $2\theta = 82.9^\circ$. The YTZP (211) showed higher intensity than the YTZP (103) in the Y-TZP powder data.

All the values of peak position (2θ) for the selected reflections for both Al_2O_3 and Y-TZP phases in starting powders are summarized in **Table 5.1**, as well as the corresponding lattice spacing calculated. The obtained values of lattice spacing from starting powders were taken as the reference stress-free lattice spacing, which was used in the following stress determination.

Fig. 5.1. The measured and fitted CW diffraction patterns of Al_2O_3 (116) and Al_2O_3 (300) for Al_2O_3 starting powder. (a) Al_2O_3 (116) reflection; (b) Al_2O_3 (300) reflection

Fig. 5.2. The measured and fitted CW diffraction patterns of YTZP (211) and YTZP (103) for Y-TZP starting powder. The peak separation was achieved, as shown in green lines.

Table 5.1. The stress-free peak information of the selected hkl reflections in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials system, obtained from Al_2O_3 powder and Y-TZP powder data: peak position, 2θ , and stress-free lattice spacing, d_{hkl}^0 .

	$\text{Al}_2\text{O}_3(116)$	$\text{Al}_2\text{O}_3(300)$	YTZP(103)	YTZP(211)
2θ (°)	79.926 ± 0.007	96.808 ± 0.009	82.94 ± 0.04	83.77 ± 0.02
d_{hkl}^0 (Å)	1.6037 ± 0.0001	1.3773 ± 0.0001	1.5550 ± 0.0007	1.5430 ± 0.0003

Through-thickness strain scanning was carried out on the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ bulk samples (thickness of 5 mm) in order to obtain the strain/stress profile. **Fig. 5.3** shows a 3D contour of the combined through-thickness scanning profiles of

$\text{Al}_2\text{O}_3(116)$ peak on the A-5YTZP (slip) sample, where the x axis is the detected peak position 2θ , the y axis corresponds to a series of scans (through thickness of samples), and the z axis is the diffraction intensity. Constant intensities were observed when the scan points were inside the bulk samples, indicating the homogenous of composition and distribution in materials. When the intensity decreases, this means that the scanning points were well out of the specimens, and this allows us to precisely position the specimen.

Fig. 5.3. A 3D contour of the combine of through-thickness scanning profiles of $\text{Al}_2\text{O}_3(116)$ peak in A-5YTZP (slip) sample.

As mentioned previously, there are two available peaks of Al_2O_3 phase near $2\theta \approx 90^\circ$, $\text{Al}_2\text{O}_3(116)$ and $\text{Al}_2\text{O}_3(300)$. The reflection of $\text{Al}_2\text{O}_3(116)$ was selected for the stress measurement in A-5YTZP composites, due to its narrow peak width and the strong intensity. With the increase in Y-TZP content, the peak of $\text{Al}_2\text{O}_3(300)$ showed a better signal comparing it with the $\text{Al}_2\text{O}_3(116)$. To determine peak position accurately and measure reliable residual stress, therefore, in A-40YTZP composites, the $\text{Al}_2\text{O}_3(300)$ was selected for scanning.

Fig. 5.4. The representative diffraction patterns of selected reflections of the Al_2O_3 and YTZP phases in A-5YTZP composites, regardless of the direction (in-plane and normal) and manufacturing techniques (tape casting and slip casting). The measured profiles are in scatter plots, and fitted profiles are in blue solid line. (a) $\text{Al}_2\text{O}_3(116)$ reflection (b) YTZP(211) peak, neighboring a weak peak of YTZP (103). The peak separation is shown in green lines.

Comparing the diffraction profiles obtained from in-plane and normal directions in the same sample, there was not much difference observed. Furthermore, with the same Y-TZP content in A/Y-TZP composites, the diffraction profiles between the tape casting sample and the slip casting samples were very similar. The representative diffraction patterns of the selected reflections of the Al_2O_3 and Y-TZP phases in A-5YTZP and A-40YTZP composites were presented in **Fig. 5.4** and **Fig. 5.5**, respectively, regardless of the direction (in-plane and normal) and manufacture techniques (tape casting and slip casting). Good fitting was achieved for all selected reflections, as can be seen from the measured (scatter plots) and fitted profiles (blue solid line).

Fig. 5.5. The representative diffraction patterns of selected reflections of Al_2O_3 and YTZP phases in A-40YTZP composites, regardless of the direction (in-plane and normal) and manufacturing techniques (tape casting and slip casting). (a) Al_2O_3 (300) reflection (b) YTZP(211) peak and a neighboring peak of YTZP (103). The peak separation is shown in green lines.

Peak information (e.g. peak position 2θ , peak intensity and peak width FWHM, etc.) was accessed after fitting. The d-spacing corresponding to each reflection was then calculated according to Eq. (3.16) in section 3.5.1.2. Taking the average values from the valid through-thickness scans, the peak information obtained for both Al_2O_3 and Y-TZP phases was given out in **Table 5.2** and **Table 5.3**, respectively. Due to the YTZP(103) signal being too weak in A-5YTZP composites, it was difficult to determine the peak information accurately. Therefore, in **Table 5.3** there is only the information on YTZP(211) is given out for A-5YTZP composites.

Table 5.2. The peak information of the studied reflections of the Al_2O_3 phase in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites: peak position 2θ , d-spacing d_{hkl} , peak intensity and the peak width FWHM.

A-5YTZP										A-40YTZP				
Casting methods	Measurement Direction	Al ₂ O ₃ (116)				Al ₂ O ₃ (300)								
		2θ (°)	d _{hkl} (Å)	FWHM	Intensity	2θ (°)	d _{hkl} (Å)	FWHM	Intensity					
Slip casting	In-plane	79.954 ±0.005	1.60316 ±0.00009	0.34 ±0.01	48 ±5	96.96 ±0.01	1.3756 ±0.0001	0.96 ±0.05	54 ±1					
	Normal	79.954 ±0.004	1.60316 ±0.00007	0.34 ±0.02	53 ±9	96.98 ±0.09	1.376 ±0.001	1.0 ±0.1	52 ±7					
Tape casting	In-plane	79.950 ±0.005	1.60322 ±0.00008	0.35 ±0.01	45 ±7	96.94 ±0.02	1.3759 ±0.0003	1.0 ±0.1	55 ±2					
	Normal	79.957 ±0.006	1.60311 ±0.00009	0.35 ±0.01	52 ±10	96.95 ±0.08	1.3758 ±0.0008	1.0 ±0.1	51 ±6					

Table 5.3. The peak information of the studied reflections of the Y-TZP phase in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites: peak position 2θ , d-spacing d_{hkl} , peak intensity and the peak width FWHM.

Samples	Measurement Direction	Y-TZP (211)				Y-TZP (103)			
		2θ (°)	d_{hkl} (Å)	FWHM	Intensity	2θ (°)	d_{hkl} (Å)	FWHM	Intensity
A-5YTZP (slip)	In-plane	83.44 ±0.01	1.5478 ±0.0002	0.41 ±0.03	46 ±3				
	Normal	83.45 ±0.01	1.5476 ±0.0002	0.45 ±0.06	42 ±7				
	In-plane	83.45 ±0.01	1.5476 ±0.0001	0.44 ±0.03	46 ±3				
A-5YTZP (tape)	Normal	83.44 ±0.01	1.5477 ±0.0002	0.46 ±0.04	37 ±6				
	In-plane	83.66 ±0.01	1.5444 ±0.0002	0.89 ±0.08	57 ±2	82.55 ±0.03	1.5613 ±0.0004	0.7 ±0.2	24 ±4
	In-plane	83.69 ±0.03	1.5440 ±0.0004	0.82 ±0.05	52 ±8	82.65 ±0.05	1.5598 ±0.0008	0.8 ±0.1	28 ±2
A-40YTZP (slip)	Normal	83.68 ±0.02	1.5440 ±0.0003	0.78 ±0.03	53 ±8	82.58 ±0.05	1.5609 ±0.0008	0.74 ±0.08	23 ±6
	In-plane	83.70 ±0.03	1.5439 ±0.0005	0.83 ±0.07	48 ±7	82.66 ±0.06	1.5597 ±0.0008	0.8 ±0.1	22 ±5
	Normal	83.70 ±0.03	1.5439 ±0.0005	0.83 ±0.07	48 ±7	82.66 ±0.06	1.5597 ±0.0008	0.8 ±0.1	22 ±5

*In A-5YTZP composites, the signal of Y-TZP(103) was too weak to be accurately determine its peak information.

5.1.2 Residual stress determination

As described in section 3.5.1.2, with the obtained lattice spacing d_{hkl} for each reflection studied, the residual strain can be determined by Eq. (3.17). The residual strain profiles for Al_2O_3 and Y-TZP phase along the sample thickness are detailed in **Fig. 5.6** and **Fig. 5.7**, both for the conventional slip casting and the novel tape casting route. As can be seen, for all the studied A/Y-TZP materials, strain in Al_2O_3 matrix was negative and that in the Y-TZP second phase was positive strain. As regards the same Y-TZP(211) reflection, as the Y-TZP content increases the tensile strain on Y-TZP obviously decreases.

Fig. 5.6. Through-thickness residual strain profiles in A-5YTZP and A-40YTZP composites manufactured by the conventional slip casting, both in the in-plane and normal directions.

Fig. 5.7. Through-thickness residual strain profiles in A-5YTZP and A-40YTZP composites manufactured by the novel tape casting technique, both in the in-plane and normal directions.

Table 5.4. The diffraction elastic constants (DEC) values used for residual stress calculation in CW neutron diffraction measurement.

	$\text{Al}_2\text{O}_3(116)$	$\text{Al}_2\text{O}_3(300)$	YTZP(211)	YTZP(103)
S_1^{hkl} Kroner ($\text{MPa}^{-1} \cdot 10^{-6}$)	-0.52456	-0.52456	-1.609729	-1.189855
$1/2 S_2^{hkl}$ Kroner ($\text{MPa}^{-1} \cdot 10^{-6}$)	2.981942	2.981942	6.36058	5.100957
E_{hkl} (GPa)	394	418	210	255
ν_{hkl}	0.213	0.230	0.327	0.347

Residual stresses can be calculated from residual strains using Hooke's law, according to Eqs.(3.35) and (3.36) in the previous section. The diffraction elastic

constants (DEC), which are specific for each lattice plane of Al_2O_3 (hkl) and Y-TZP (hkl), were needed and obtained by the IsoDEC program [165, 166], following the Kröner model [167, 168]. **Table 5.4** shows the DEC values used for residual stress calculation in present work.

The through-thickness residual stress profiles are detailed in **Fig. 5.8** and **Fig. 5.9**, corresponding to samples manufactured by the conventional slip casting and the novel tape casting routes, respectively. In agreement with the behaviour of residual strain, the residual stresses are tensile in the Y-TZP particles and increase as its volume fraction decreases. For the Al_2O_3 matrix, residual stress is compressive and increases with the Y-TZP volume fraction. It can be seen that the differences between the residual stresses in the in-plane and normal directions are not obvious, which lie within the experimental error in all cases.

Fig. 5.8. Through-thickness residual stress profiles in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites manufactured by the conventional slip casting technique, reinforced with 5 and 40 vol.% Y-TZP, both in the in-plane and normal directions.

Fig. 5.9. Through-thickness residual stress profiles in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites manufactured by the novel tape casting technique, reinforced with 5 and 40 vol.% Y-TZP, both in the in-plane and normal directions.

The through-thickness strain scanning was used to check the homogeneity of the stress state within the samples (5 mm thickness). The stress profiles obtained are rather flat in most samples, except those in A-40YTZP(tape) composites which showed some variation. It might be due to some problem in the tape casting procedure for this particular sample, for instance, the defects in interface between individual tapes. However, the gauge volume used in strain scanning, which was $1 \times 1 \times 10 \text{ mm}^3$, always encompasses at least three individual tapes (typical thickness around $500 \text{ }\mu\text{m}$) in the sample manufactured by tape casting. Therefore, stress gradients close to the interface between individual tapes cannot be detected sensitively. As previously described in the fracture surface observation in **Fig. 4.8** (in section 4.5.1.2), part of the tape interfaces could be observed in tape casting samples, indicating the possible existence of defects in tape interfaces. It might explain the variation in stress profiles in the A-40YTZP(tape) sample.

For the composites with the 5 vol.% Y-TZP addition, the residual stresses are very similar in the sample obtained by conventional slip casting and that

manufactured by the novel tape casting route. Taking into account the in-plane and normal directions, in A-5YTZP composites, the average residual stress in the Y-TZP phase is about 1850 ± 140 MPa, whereas in the alumina matrix it is -208 ± 60 MPa. Small difference was detected in the residual stresses in the slip and tape casting samples for the A-40YTZP composites. The average stress in the Y-TZP particles is around 580 ± 150 MPa in the sample manufactured by slip casting and 520 ± 150 MPa in that manufactured by tape casting. In the alumina matrix, the average value of compressive stresses is -770 ± 100 MPa in the slip casting sample and -740 ± 100 MPa in the tape casting one.

The residual stresses in the Y-TZP particles and Al_2O_3 matrix are not independent but governed by the equilibrium equation [154]:

$$f_A \sigma_A + f_{\text{YTZP}} \sigma_{\text{YTZP}} = 0 \quad (5.1)$$

where f_A , f_{YTZP} are the volume fractions of Al_2O_3 matrix and Y-TZP particulates in composites, respectively; and σ_A , σ_{YTZP} are the corresponding phase stresses. This equation can be used to check the equilibrium condition within the sample. The through-thickness values of $f_A \sigma_A + f_{\text{YTZP}} \sigma_{\text{YTZP}}$ were also plotted in **Fig. 5.8** and **Fig. 5.9** for slip and tape casting samples. It can be seen that the static equilibrium condition in A-5YTZP composites is approximately fulfilled at all measurement points, demonstrating that the macro-residual stresses are negligible, irrespective of the processing route. However, in the composite with 40 vol.% Y-TZP, the obtained value of $f_A \sigma_A + f_{\text{YTZP}} \sigma_{\text{YTZP}}$ was around -200 MPa, implying the macrostress was not negligible.

As discussed in section 4.1, during the manufacturing process, no transformation from tetragonal zirconia to monoclinic zirconia ($t \rightarrow m$ transformation) occurred in these materials. The micro-residual stresses induced in both Al_2O_3 matrix and Y-TZP particles were mainly from the thermal expansion mismatch between them ($\alpha_{A, 25-1000^\circ\text{C}} = 8.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ [78], $\alpha_{\text{Y-TZP}, 25-1000^\circ\text{C}} = 10.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ [79]), arising during the sintering and cooling process [122, 219]. The residual stress states detected in the slip casting sample and tape casting samples were quite similar, even though there were some small differences between the slip casting sample and the tape casting samples in A-40YTZP composites, but it is not remarkable. It implies that, at least for the pressure levels (18 MPa) used in the proposed novel tape casting processing, the green state stacking of tapes does not lead to residual stress development during sintering. This behavior is easily

explained because any kind of stress imposed during pressing at room temperature will relax at high temperature, where diffusional mechanisms act on the material. In fact, only microstructural defects imposed by high pressures will remain in the material after sintering due to the memory effect in ceramic processing. Therefore, in this work, the non-zero macro-stresses detected in A-40YTZP composites were possibly mainly related to the composition and microstructural effects, but not to the green processing studied (slip and tape casting). More investigations need to be done for this topic.

As a brief summary, the constant-wavelength (CW) neutron diffraction was used to measure detailed residual stress profiles in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ ceramic composites manufactured by traditional slip casting and by a novel tape casting route. Stresses were measured in both alumina and zirconia phases, and in two directions, in-plane and normal. The profiles obtained are rather flat in most samples. For the composite with 5 vol.% zirconia only micro-residual stresses, compressive in the alumina matrix (around -208 ± 60 MPa) and tensile ones in the Y-TZP particles (around 1850 ± 140 MPa), develop in this material due to thermal expansion mismatch between the phases, irrespective of the orientation (in-plane and normal) and of the manufacturing process (conventional slip casting or the novel tape casting). As the addition of Y-TZP second phase increasing, the residual stresses (absolute value) in Y-TZP decreased and those in the alumina matrix increased. Ignoring the small differences in residual stress values between the slip casting and the tape casting routes in A-40YTZP composites, the approximate values of the compressive stresses in the Al_2O_3 matrix were around -770 ± 100 MPa and the tensile ones in Y-TZP particles were around 580 ± 150 MPa.

5.2 TOF neutron diffraction

Due to the thermal-elastic anisotropy in crystal and complexity of microstructure, residual strain/stress from single diffraction peak measurement (e.g. in previously described measurements by CW neutron diffraction) cannot be treated exactly as bulk behavior [220]. In order to access more reliable and detailed RS information on the behavior of both the bulk components and micro-scales, as well as monitoring the phase composition and crystal structures in sintered ceramics, the time-of-flight (TOF) neutron diffraction technique was used.

Combining with the well-known whole profile structure refinement method—Rietveld refinement [11], information on stresses can be extracted from the whole

TOF diffraction spectra, mainly from the following aspects: (i) the variation of unit cell parameters compared with strain-free crystal, which could be used to determine the average stress of phases in detected areas (type II stresses) and estimate the macrostresses at the continuum scale (type I stresses); (ii) individual peak center shift, corresponding to intergranular stress state within a single phase; (iii) peak broadening [33, 170, 221], which is associated with non-uniform micro-strain at the atomic scale (type III stresses), as well as the small coherently diffracting domain size.

In this part of work, the uniform and non-uniform residual stress effects were precisely detected in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites with a different Y-TZP content and green processing (the novel tape casting and conventional slip casting). The uniform RS data obtained was compared to data available in the literatures and to theoretical model estimation. Multi-phase qualitative and quantitative analyses, as well as crystal structure determination was achieved in Rietveld refinement. Microstructural information (domain size and crystal microstrain) was accessed by peak broadening analysis.

5.2.1 Neutron diffraction patterns and Rietveld analysis

The whole diffraction spectrum was collected by TOF neutron diffraction scanning. Rietveld refinement was carried out for the whole diffraction profile fitting and analysis in the program TOPAS-Academic V5 [47]. As introduced in section 3.4.1.2, after the instrument calibration procedure on the data of standard CeO_2 powder, the instrument-dependent diffractometer constants and profile parameters were obtained, which were fixed and used for the following refinements of the alumina and zirconia starting powders and $\text{Al}_2\text{O}_3/\text{Y-TZP}$ bulk samples.

5.2.1.1 Diffraction profiles of powders

The data of alumina starting powder, as hexagonal $\alpha\text{-Al}_2\text{O}_3$ phase (space group $R\bar{3}c$, $a=b=4.7602$ Å, $c=12.9933$ Å), were analyzed by Rietveld refinement. Diffraction profiles of alumina powder, as well as its fitting profiles (red line) by Rietveld refinement, are shown in **Fig. 5.10**. The difference plots between the observed and calculated intensities are shown as a grey line, below the diffraction spectra. Good fitting was achieved with the weighed residual error $R_{\text{wp}}=6\%$.

Fig. 5.10. The TOF neutron diffraction patterns of Al_2O_3 starting powders (blue line), as well as its fitting profiles (red line) by Rietveld refinement.

It is well known that zirconia is a polymorphic material which has three typical structural forms: monoclinic (m), tetragonal (t), and cubic (c) [62, 63]. In consideration of the complex polymorph of ZrO_2 [67], especially the possible $t - m$ transformation during the manufacturing process, Rietveld refinements trials have been carried out for zirconia starting powder and A/Y-TZP bulk samples, with crystal structure information of tetragonal (t) Y_2O_3 -doped ZrO_2 (Y-TZP) [158], monoclinic (m) ZrO_2 [67] and cubic (c) Y_2O_3 -doped ZrO_2 [67] being introduced simultaneously. The fitting results confirmed no existence of cubic zirconia phase in both Y-TZP starting powder and A/Y-TZP composites. Around 70 vol. % tetragonal Y-TZP and 30 vol. % m- ZrO_2 were detected in zirconia starting powder, as in the diffraction profile shown in **Fig. 5.11**. These results on TOF neutron diffraction are in good consistence with the XRD analysis (section 3.2.1, **Fig. 3.1**).

However, in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites, only the phases of $\alpha\text{-Al}_2\text{O}_3$ matrix and tetragonal Y-TZP were detected, without m- ZrO_2 . Therefore, in this work, the Rietveld refinements of zirconia starting powder were done with both m- ZrO_2 and tetragonal Y-TZP crystal structures. All A/Y-TZP composites were studied by using a two-phase model consisting of the hexagonal $\alpha\text{-Al}_2\text{O}_3$ phase and tetragonal Y-TZP phase.

Fig. 5.11. The time-of-flight neutron diffraction patterns with Rietveld refinement for Y-TZP starting powders. Tetragonal Y-TZP (*t*) and monoclinic ZrO_2 (*m*) were detected in zirconia starting powder, with the corresponding diffraction peaks being identified at the bottom of profiles with blue tick marks and black ones, respectively.

5.2.1.2 Diffraction profiles of bulk samples

As regards the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ bulk sample, no obvious differences were observed between the TOF diffraction profiles of slip casting samples and tape casting samples with the same Y-TZP vol. %. In addition, at the same scanning point, differences between the spectra of in-plane and normal direction (measured at $2\theta = \pm 90^\circ$) are insignificant, which indicates almost homogenous phase and microstructure distribution in materials. The representative diffraction patterns of the A/Y-TZP composites were presented as a function of addition of Y-TZP reinforcement (5 vol.% and 40 vol.%, respectively), irrespective of the manufacturing routes (slip and tape casting) and measurement directions (in-plane and normal). **Fig. 5.12** and **Fig. 5.13** show the representative diffraction patterns for the A-5YTZP(slip) composites and A-40YTZP (tape) composites, respectively. The raw data observed is shown as a blue line and the associated calculated profile is a red line, overlapping the blue observed profiles. The individual peaks of $\alpha\text{-Al}_2\text{O}_3$ and Y-TZP phases were identified with blue and black tick marks at the bottom of the profiles, respectively. The difference plots between the observed and calculated intensities are shown as a grey line, below the spectra. As observed in **Fig. 5.12** and

Fig. 5.13 almost flat difference lines were obtained for both A-5YTZP and A-40YTZP composites. Good fits were achieved for all reference powders and bulk samples, with the weighed residual error R_{wp} ranging from 4% to 10%.

The Rietveld refinement of a two-phase model consisting of α - Al_2O_3 phase and tetragonal Y-TZP phase was highly satisfactory for all A/Y-TZP composites bulk samples, without evidence of the m - ZrO_2 phase, as can be seen in **Fig. 5.12** and **Fig. 5.13**. This shows that almost all the monoclinic phase in the zirconia starting powder was transformed to tetragonal structure during heating at high temperature (at around 1170 °C) [64]. No transformation from tetragonal zirconia to monoclinic zirconia ($t \rightarrow m$ transformation) occurred during the cooling process from the high sintering temperature to room temperature, in agreement with the data published [222, 223]. This could be explained by the stabilizing action of Y_2O_3 on zirconia, as well as the restraint from phase-change volume expansion by Al_2O_3 matrix during cooling. As a consequence, the existence of residual stresses between Al_2O_3 matrix and Y-TZP inclusion were anticipated.

By comparing the diffraction spectra of A-5YTZP composites (**Fig. 5.12**) and A-40YTZP composites (**Fig. 5.13**), as the zirconia content increases, the peak intensities of Y-TZP increase and those of the Al_2O_3 matrix reduce.

Phase quantities corresponding to the measured gauge volumes were evaluated in Rietveld refinement, and the volume fraction is shown in the upper right of the profile fitting window (e.g. **Fig. 5.12** and **Fig. 5.13**). Almost constant Y-TZP contents were detected in different scanning positions of the same sample, with 5 ± 2 vol. % in A-5YTZP composites and 40 ± 3 vol. % in A-40YTZP composites, which were very close to the nominal values.

Fig. 5.12. The representative TOF neutron diffraction patterns with Rietveld refinement for A-5Y-TZP (slip) samples. Individual peaks of Al_2O_3 and Y-TZP are marked at the bottom of profiles with blue tick marks and black ones, respectively. Investigated reflections are marked above the peaks, with ★ for Al_2O_3 and * for Y-TZP.

Fig. 5.13. The representative TOF neutron diffraction patterns with Rietveld refinement for A-40YTZP (tape) samples. Investigated reflections are marked above the peaks, with ★ for Al_2O_3 and * for Y-TZP. Detailed fittings were shown at (a) $\text{tof} = 32300 \mu\text{s}$ $\sim 34300 \mu\text{s}$ with reflections of Y-TZP (200) and (112), and (b) $\text{tof} = 32300 \mu\text{s} \sim 44300 \mu\text{s}$ with reflections of Al_2O_3 (113).

5.2.2 Crystal structures

With Rietveld refinement of the neutron diffraction data, the crystal structures of α -Al₂O₃ and tetragonal Y-TZP in stress-free starting powders and in A/Y-TZP composites were obtained.

Table 5.5 summarizes the average values of the refined lattice parameters of α -Al₂O₃ (a , c) and tetragonal Y-TZP (a_t , c_t) over different scanning points in each sample, with the standard deviations in brackets. Comparing the slip casting and the tape casting samples with the same Y-TZP contents, no great obvious difference can be seen from the unit-cell parameters for both α -Al₂O₃ and tetragonal Y-TZP crystallites, with the exception of the Y-TZP in A-5YTZP samples. Due to the small fraction of Y-TZP inclusion in A-5YTZP composites, the lattice parameters of Y-TZP were not easy to be precisely determined, leading to relatively higher variance in lattice parameters over different scanning points in the same bulk sample, as manifested by the higher variance errors in brackets.

It was discovered that the crystal structures of Al₂O₃ and tetragonal Y-TZP phases varied from starting powders to A/Y-TZP bulk samples after the manufacturing process (including green processing, sintering, etc.), as a function of Y-TZP vol. %. As can be seen from **Table 5.5**, in sintered A-5YTZP composites the a value of α -Al₂O₃ crystals decreased slightly but the c value increased, comparing it with starting Al₂O₃ powder. A compressive strain was anticipated in the direction of the a axis ($\varepsilon_a < 0$) in Al₂O₃, as well as tensile strain along in the direction of the c axis ($\varepsilon_c > 0$). However, as addition of Y-TZP increased to 40 vol. %, all the cell parameters (a and c) of α -Al₂O₃ were decreased. More shrinkage in c -axis was observed than in a -axis, implying $\varepsilon_a, \varepsilon_c < 0, |\varepsilon_a| < |\varepsilon_c|$.

Table 5.5. The unit-cell parameters (Å) of α -Al₂O₃ phase and Y-TZP phase obtained from Rietveld refinement of starting powders and A/Y-TZP bulk composites (average values over different scanning points in each sample)

Sample	α -Al ₂ O ₃ phase				Tetragonal Y-TZP phase			
	In-plane		Normal		In-plane		Normal	
	a	c	a	c	a _t	c _t	a _t	c _t
Al ₂ O ₃ powder	4.75973	12.99355	4.75997	12.99315	-	-	-	-
Y-TZP powder	-	-	-	-	3.60793	5.17255	3.60825	5.17230
A-5YTZP (slip)	4.7586 (2)	12.9966 (5)	4.7583 (1)	12.9965 (6)	3.6095 (10)	5.1910 (20)	3.6092 (12)	5.1892 (18)
A-5YTZP (tape)	4.7587 (1)	12.9966 (7)	4.7584 (1)	12.9965 (4)	3.6099 (10)	5.1900 (20)	3.6094 (9)	5.1868 (16)
A-40YTZP (slip)	4.7571 (2)	12.9911 (8)	4.7572 (2)	12.9915 (9)	3.6075 (4)	5.1856 (6)	3.6069 (2)	5.1845 (7)
A-40YTZP (tape)	4.7571 (2)	12.9907 (7)	4.7573 (2)	12.9912 (8)	3.6074 (5)	5.1853 (8)	3.6066 (2)	5.1846 (7)

As regards the tetragonal Y-TZP phase, even though the crystal structures obtained were relatively unstable due to their small addition in A-5YTZP samples, a remarkable increase in the c_t value in tetragonal Y-TZP was exhibited, as well as in A-40YTZP composites. A slight increase in the a_t value of the Y-TZP crystals was detected in A-5YTZP samples, whereas it decreased in the A-40YTZP composites.

This behavior can be understood by considering the thermal expansion anisotropy of each phase and thermal expansion mismatch between phases, as well as the microstructure characteristics of the composites. According to the microstructure observation, in A-5YTZP composites (Fig. 4.1(a)), fine Y-TZP particles were dispersed and surrounded by randomly oriented large-sized alumina matrix grains. For the Al₂O₃ matrix, most particle surfaces were interconnected with Al₂O₃ grains themselves, leading to the predominant effect of anisotropic thermal expansion of α -Al₂O₃ ($\alpha_{a,25-1000^\circ\text{C}} = 8.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, $\alpha_{c,25-1000^\circ\text{C}} = 9.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) [78] rather than the thermal expansion mismatch with Y-TZP particulates. However, with the increase in the Y-TZP content, the grain size of the alumina matrix decreased; several Y-TZP grains piled together and even surrounded the alumina grains (Fig. 4.1(b)). Consequently, effects from Y-TZP second phase to Al₂O₃ matrix were significantly enhanced. As a result of the thermal expansion mismatch between the Al₂O₃ matrix ($\alpha_{a,25-1000^\circ\text{C}} = 8.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) [78] and the Y-TZP particles ($\alpha_{Y-TZP,25-1000^\circ\text{C}} = 10.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) [79], the Al₂O₃ matrix grains were compressed and lattice parameters decreased. On the other hand, for the Y-TZP particles, most of restraints came from the Al₂O₃ matrix in A-5YTZP composites. By increasing the Y-TZP addition, the contact between the Y-TZP and the Al₂O₃ was reduced, and there was an enhanced contact between the Y-TZP grains. As a consequence of the reduced thermo-elastic mismatch effects from Al₂O₃ matrix, reduced RS on the Y-TZP phase were anticipated.

It is usually used the tetragonality (c/a) to represent the tetragonal degree of a tetragonal crystal. As regards the tetragonal Y-TZP, the tetragonality of Y-TZP crystal in each of the A/Y-TZP composites was analyzed. Due to the tetragonal Y-TZP phase is indexed according to the $Z=2$ cell, to compare with the more ordinarily used fluorite-like (pseudo-cubic, $Z=4$) cell, the a_t lattice parameter must be multiplied by $\sqrt{2}$ [224, 225]. Thus the tetragonality is defined as $c_t/(\sqrt{2}a_t)$, where a_t and c_t are the determined lattice parameters of Y-TZP.

The evolution of tetragonality in the Y-TZP crystal varies from 1.0138 in the starting zirconia powder to 1.0166 (4) in both of A-5YTZP and A-40YTZP

composites, as calculated. In general, higher tetragonality contributes to a less stable material characterized by an increased martensitic start (Ms) temperature [226].

The Y_2O_3 concentration in the remaining tetragonal ZrO_2 phase could be estimated based on tetragonality ($c_t/(\sqrt{2}a_t)$) using the following equation [227]:

$$YO_{1.5}(\text{mol \%}) = \frac{1.0223 - \frac{c_t}{\sqrt{2}a_t}}{0.001319} \quad (5.2)$$

It was discovered that in zirconia starting powder, the calculated Y_2O_3 concentration in tetragonal Y-TZP phase, as a value of 3.2 mol %, was more or less equal to that of the ideal one (3 mol %). But in A/Y-TZP bulk samples, the calculated Y_2O_3 mol % decreased to around 2.16 mol %.

5.2.3 Stress determination

With the TOF entire diffraction spectrum, residual stresses behavior can be estimated either from lattice parameters variation or individual hkl peaks shifts. The former represented the average stress behaviors of individual phase, named as mean phase stress, and the latter is stress in individual grain, named as peak-specific residual stresses.

5.2.3.1 Mean phase stresses

In TOF measurement, the mean phase stresses of both Al_2O_3 and Y-TZP phases, as the averaged stresses for each phase over a large number of randomly oriented grains within the gauge volume area, were calculated using the change of average lattice parameters for Al_2O_3 and Y-TZP phases, as shown by Eqs. (3.27)-(3.33). The through-thickness mean phase profiles of the stresses along the in-plane and normal directions were detailed for both the conventional slip casting (**Fig. 5.14**) and the novel tape casting routes (**Fig. 5.15**). In this case the error bars of the mean phase stresses related to the statistical uncertainties of the determined lattice parameters are smaller than the size of the symbols used in the graphs.

As expected [122, 223], the residual stresses were compressive in the Al_2O_3 matrix and tensile in the Y-TZP particles, due to the lower thermal expansion

coefficient of the Al_2O_3 matrix as compared with the Y-TZP particles. Quite homogeneous stress profiles through sample thickness were found for both phases in each specimen, as can be seen in **Fig. 5.14** and **Fig. 5.15**, especially in the Al_2O_3 matrix, which agrees with a homogenous distribution of residual stress within the samples. For the sample manufactured by tape casting, each measurement point always encompasses at least three individual tapes (typical thickness of around 500 μm), due to the gauge volume used ($1 \times 1 \times 10 \text{ mm}^3$). Consequently, stress gradients close to the interface between individual tapes cannot be resolved, which explains the flat profiles observed.

No significant differences can be observed between composites with the same composition from conventional slip casting (**Fig. 5.14**) and the novel tape casting routes (**Fig. 5.15**), according to the stress behavior of Al_2O_3 matrix and Y-TZP particles in composites. This seems to indicate that the low pressure (18 MPa) used for stacking tapes in the novel tape casting green process did not lead to additional macro-residual stresses after sintering. Consequently, the micro-residual stresses in both phases were mainly induced by thermal and elastic mismatches between phases.

However, the mean phase stresses changed as a function of the Y-TZP content in composites. Irrespective of the manufacturing process (slip casting or tape casting), as the Y-TZP content increases from 5 vol. % to 40 vol. %, the tensile stresses in the Y-TZP particles decreased from an average value of 740 MPa in A-5YTZP composites to approximately 400 MPa in A-40YTZP composites. On the other hand, the compressive stresses in the Al_2O_3 matrix increase (in absolute value) from an average value of -70 MPa in the A-5YTZP composites to approximately -320 MPa in the A-40YTZP composites. This behavior agrees with the trends observed in the literature [122].

By comparing these values from the TOF measurement with those obtained from single reflection scanning by constant-wavelength neutron diffraction (section 5.1.2), an obvious difference was observed. The difference may be due to the elastic anisotropy associated to the peaks measured in CW neutron diffraction test. It is well known that in single peak measurements, the magnitude of the residual stress calculated is highly dependent on the particular reflection used for the analysis. On the other hand, the results obtained in this paper are similar to those reported in [202], where residual stresses were determined by piezospectroscopy in the same materials investigated in this work. In [202], the hydrostatic component of the residual stresses in both phases was calculated from experimental measurements in the alumina phase and by imposing the static equilibrium condition (Eq. 5.1) in the

zirconia phase. The residual stresses reported in [202] for the A-5YTZP composites are equal to -50 MPa for the alumina phase, whereas in our case the average value is around -70 MPa. Taking into account that the typical error associated to residual stress measurements is approximately 20 MPa, both results appear quite close. If the static equilibrium condition is applied, in the case of the A-5YTZP (95% alumina, 5% zirconia) this error would translate into approximately 200 MPa when the residual stresses in the zirconia phase are calculated. This would explain the difference between our results in the zirconia phase (750 MPa) and those reported in [202] for the A-5YTZP composite in the same phase (950 MPa).

In addition, the measurements of residual stresses along the in-plane and normal directions were used to detect possible orientation effects in samples due to the manufacturing routes. No significant differences were found between directions for the Al_2O_3 matrix, especially in A-40YTZP composites, although slightly higher tensile stresses in the in-plane direction than in the normal direction were detected in the zirconia phase.

Fig. 5.14. Mean phase stress profiles for Al_2O_3 (Δ) and Y-TZP ($\square$) phase along the thickness of A/Y-TZP (slip casting) bulk samples, both in the in-plane and normal directions. The values of $f_A \sigma_A + f_{\text{YTZP}} \sigma_{\text{YTZP}}$ were presented without any line.

Fig. 5.15. Mean phase stress profiles for Al_2O_3 (Δ) and Y-TZP ($\square$) phase through the thickness of A/Y-TZP(tape casting) bulk samples, both in the in-plane and normal directions. The values of $f_A\sigma_A + f_{\text{YTZP}}\sigma_{\text{YTZP}}$ were presented without a line.

In this case, residual stresses in a particulate-reinforced composite may arise during cooling from the sintering temperature, due to the mismatch of thermal expansion and elastic constants between the matrix and the particulates [228]. In addition, as explained above, no $t \rightarrow m$ transformation occurred in zirconia during the cooling process, and consequently, residual stresses in the A/Y-TZP composites were supposed to have a thermal origin.

The modified Eshelby model proposed by Taya *et al.* [228] was used to estimate the residual stresses in the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites, in order to confirm the diffraction measurement results. As the densities were close to the theoretical values, the composites were assumed to have no voids and consisting of two phases: an α - Al_2O_3 matrix with its volume fraction of f_m and the Y-TZP reinforcement particulates with a volume fraction f_p . The thermal residual strain due to the mismatch in thermal expansion coefficients of matrix and particulates, called CTE misfit strain ε^* is given by:

$$\varepsilon^* = \int_{T_p}^{T_{Room}} (\alpha_p - \alpha_m) \delta dT \quad (5.3)$$

where α_m and α_p are the thermal expansion coefficients of the Al_2O_3 matrix and the Y-TZP particulates, respectively, δ is the isotropic tensor (Kronecker's delta), T_{Room} are the room temperature and T_p are the effective freezing temperature [229], which was estimated to be 1200 °C in the present $\text{Al}_2\text{O}_3/\text{Y-TZP}$ system [230]. As highly dense composites, the isotropic average stress fields in the particulate, σ_p , and in the matrix, σ_m , can be estimated as [228]:

$$\frac{\sigma_p}{E_m} = \frac{-2f_m\beta\varepsilon^*}{A} \quad (5.4)$$

$$\frac{\sigma_m}{E_m} = \frac{2f_p\beta\varepsilon^*}{A} \quad (5.5)$$

where $A = f_m(\beta + 2)(1 + \nu_m) + 3\beta f_p(1 - \nu_m)$, $\beta = \frac{(1 + \nu_m)}{(1 - 2\nu_p)} \left(\frac{E_p}{E_m} \right)$, ε^* is the CTE misfit strain, f_i , E_i and ν_i are the volume fraction, elastic modulus and Poisson's ratio of i phase, where $i = m$ and P represents the Al_2O_3 matrix and Y-TZP particulates, respectively.

Based on Eq. (5.3), with $\alpha_p > \alpha_m$ in A/Y-TZP composites, the CTE misfit strain would be negative during cooling from the sintering temperature to room temperature. Consequently, tension in Y-TZP particulates and compression in the Al_2O_3 matrix were expected, in good agreement with the experimental results by neutron diffraction. Irrespective of different processing techniques and grain size effect, the average thermal residual stresses in the Y-TZP phase and the Al_2O_3 phase in the A-5YTZP and A-40YTZP composites can be estimated according to Eqs. (5.4) and (5.5):

In A-5YTZP composites: $\sigma_{\text{A-5YTZP}}^{\text{Y-TZP}} = 741 \text{ MPa}$, $\sigma_{\text{A-5YTZP}}^{\text{A}} = -39 \text{ MPa}$;

In A-40YTZP composites: $\sigma_{\text{A-40YTZP}}^{\text{Y-TZP}} = 489 \text{ MPa}$, $\sigma_{\text{A-40YTZP}}^{\text{A}} = -326 \text{ MPa}$.

A decrease in the tensile stress in the Y-TZP phase and an increase in the absolute value of the compressive stress in the Al_2O_3 matrix with the volume

fraction of Y-TZP are found, which agrees very well with the neutron diffraction experimental results.

The microstructure development should also be taken into account. As described in section 4.1 (**Fig. 4.1** and **Table 4.1**), with more zirconia content, the grain size of Al₂O₃ matrix reduced but that of the Y-TZP increased slightly. For a single Y-TZP particle, its connectivity with the Al₂O₃ matrix would be decreased but that between the Y-TZP particulates would be enhanced. The internal tensile stresses on the Y-TZP particulates, which were caused by the thermal and elastic mismatch with the surroundings, were correspondingly weakened. In contrast, the increase in Y-TZP particles would cause a separation in the Al₂O₃ matrix. For a single Al₂O₃ matrix grain, it results in more contact areas with the Y-TZP particles therefore increased thermal-elastic mismatch effect from Y-TZP particulates; consequently, compressive stress on the Al₂O₃ matrix increased.

The calculated residual stresses in the alumina matrix by using the modified Eshelby model proposed by Taya [47] were very similar to those obtained by neutron diffraction measurements in this work, especially in the A-40YTZP composites. Such a good agreement was also observed for the residual stresses in the zirconia phase in the A-5YTZP composites. As the Y-TZP content increased to 40 vol. %, the tensile residual stress in the zirconia phase obtained from neutron diffraction measurements was slightly lower than the model predictions. According to recent work by C. Exare *et al.* [231], the attrition on alumina and zirconia slurries by high energy milling will influence the stability of the different zirconia phases and generate compressive residual stresses. Although in the present work, ball milling was used, the possibility that compressive residual stresses might be generated in zirconia should not be completely ruled out, especially when the volume fraction of zirconia is increased. This, in turn, might help to explain the differences observed between the residual stresses measured in zirconia by neutron diffraction and the model predictions.

It was initially assumed the macro-residual stresses are negligible in all of the A/YTZP bulk samples since no pressure was applied during the sintering process. The equilibrium of mean phase residual stresses of the Y-TZP particles and the Al₂O₃ matrix was checked using the static equilibrium condition for residual stresses [232]:

$$f_A \sigma_A + f_{YTZP} \sigma_{YTZP} = 0 \quad (5.6)$$

where f_A , f_{YTZP} are the volume fractions of the Al_2O_3 matrix and Y-TZP in composites; and σ_A , σ_{YTZP} are the measured mean phase stress of the Al_2O_3 matrix and Y-TZP particulates, respectively.

The values of Eq. (5.6) through thickness are plotted in **Fig. 5.14** and **Fig. 5.15** for slip and tape casting samples. It can be seen that in all cases the static equilibrium condition is verified approximately.

5.2.3.2 Peak-specific residual stresses

Several hkl reflections were recorded in a TOF diffraction spectrum. Peak-specific residual stresses were accessed by measuring shifts in individual diffraction peaks. By considering the peak intensity, non-overlapping and clear shape in diffraction spectra of stress-free reference powder and composites, peaks of Al_2O_3 (300), (116), (113), (006) and Y-TZP (103), (200), (112) were selected (**Fig. 5.13**). The d-spacing of each peak was obtained after the Rietveld refinement of diffraction profiles. The stress-free lattice spacings d_0 of chosen reflections were taken from the diffraction profiles of the Al_2O_3 and the Y-TZP reference powders. The elastic lattice stresses for selected peaks were calculated following Eq. (3.33)-(3.36).

The through thickness residual stress behaviors of Al_2O_3 (300), (116), (113), (006) and Y-TZP (103), (200), (112) for all bulk samples, measured in both in-plane and normal directions, are plotted in **Fig. 5.16** and **Fig. 5.17**, respectively. Error bars corresponding to statistical uncertainties of the determined peak position were too small to be visible in the presented graphs. No remarkable difference can be observed between the slip casting and the tape casting samples under the same Y-TZP addition. Thus, the following discussion focuses on effect of the Y-TZP %.

(a)

(b)

Fig. 5.16. The through thickness residual stresses behaviors of Al_2O_3 (300), (116), (113), (006) in A/YTZP composites (blue: A-5YTZP, red: A-40YTZP), measured in both in-plane (solid line & solid symbol) and normal (dash line & open symbol) directions. (a) manufactured by slip casting; (b) manufactured by tape casting.

As can be seen from **Fig. 5.16** and **Fig. 5.17**, for both the Al_2O_3 matrix and the Y-TZP particulates, residual stresses vary along different hkl reflections. Almost flat residual stress profiles through thickness were observed for all selected individual reflections of the Al_2O_3 and the Y-TZP phases, as well as the similar stress behaviors between the in-plane and the normal directions, which indicated homogenous stress and microstructure distribution in materials.

Compressive stress developed in most of the selected hkl reflections of the Al_2O_3 phase in all studied A/Y-TZP composites, except of A (006) and A (116) in A-5YTZP sample. On the other hand, most of the selected Y-TZP reflections were in tension, with exception of Y-TZP(200) in the A-40YTZP composites in compression. It was discovered that as the Y-TZP content increased from 5 % to 40 %, the absolute values of the stresses in each selected reflections in the Al_2O_3 matrix increased and in the Y-TZP phase they decreased, consistent with their mean phase stresses behavior discussed before. The sequences of stress values of different hkl in both phases were unchanged as the Y-TZP content varied.

Fig. 5.17. The through thickness residual stresses behaviors of Y-TZP (103), (200), (112) in A/YTZP composites (blue: A-5YTZP, red: A-40YTZP), measured in both in-plane (solid line & solid symbol) and normal (dash line & open symbol) directions. (a) manufactured by slip casting; (b) manufactured by tape casting.

The results of d-spacing and calculated stresses for each reflection could be explained by an interplanar spacing calculation formula in a crystal system [233]. For hexagonal α -Al₂O₃, the relationship between the interplanar spacings (d_{hkl}) for a given plane and the lattice parameters a ($a=b$) and c could be written as:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3a^2}(h^2 + k^2 + hk) + \frac{l^2}{c^2}}} \quad (5.7)$$

As regards a specific hkl , it is obvious that the variation in the d-spacing of the Al₂O₃ planes will be mainly determined by the a and c axis of the α -Al₂O₃ crystals. According to the obtained lattice parameters in **Table 5.5**, as the Al₂O₃ powder being manufactured to A-5YTZP composites, the a axis of α -Al₂O₃ was shrunk, but its c axis was slightly extended. In this case, $d_{A(006)}^{A5YTZP} > d_{A(006)}^0$ was anticipated from Eqs.(5.7), leading to the A (006) with tension as exception in the A-5YTZP

composites. However, for the A-40YTZP composites, both the a and c axes shrank compared to the Al_2O_3 reference powder, d_{hkl} was expected to be reduced and compression took place in all selected planes. Consequently, in the studied A-5YTZP samples, tension could be detected for $00l$ reflections in Al_2O_3 .

The interplanar spacings (d_{hkl}) in the Y-TZP tetragonal crystal system is given by:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}} \quad (5.8)$$

With both the lattice parameters, a_t and c_t , of tetragonal Y-TZP in the A-5YTZP composites larger than the reference powder values (**Table 5.5**), tension was generated in all Y-TZP selected reflections. However, as the Y-TZP % increased to 40 vol. %, a_t parameter decreased slightly, thus, for all $hk0$ planes in A-40YTZP composites, compressive stresses were anticipated. This agrees well with the measured stresses of the YTZP (200) in the A-40YTZP bulk samples.

As regards a given sample, the lattice parameters for both Al_2O_3 and Y-TZP were certain. When comparing the behavior of different hkl planes in each phase, the d-spacings varied in terms of Miller indices hkl . That's why the order of strain/stress values within a set of hkl was kept the same in each sample.

The average residual stress values of selected peaks for both the Al_2O_3 and the Y-TZP phases were given in **Table 5.6** and **Table 5.7**, as well as the corresponding mean phase stresses, as reported in section 5.2.3.1. It is accepted that peak-specific residual stress behaviors are closely related to the anisotropic CTE in each phase. Due to the different thermal expansions and elastic properties in each hkl direction, for the same sample and same phase, the residual stresses values obtained are different from each reflection. It reveals that the sign and the magnitude of the residual stress values depend greatly on the reflection used for analysis. This is a warning for residual stress measurements and analysis with single peak reflections in complex materials.

As can be seen, for both of the mean phase stress and peak-specific residual stress in Al_2O_3 /Y-TZP bulk samples, no obvious difference was observed due to sample orientation (in-plane and normal directions) and the manufacturing processes (the novel tape casting and the conventional slip casting). The hydrostatic stress state was achieved in the studied Al_2O_3 /Y-TZP composites. It could be concluded that the

novel tape casting process does not change the residual stresses state, which is mainly associated to thermal residual strain.

Table 5.6. The average residual stress values of selected peaks for Al₂O₃ phase, comparing it with the corresponding mean phase stresses, as previously reported in section 5.2.3.1.

Sample	$\sigma_{\text{Al}_2\text{O}_3}$ (MPa)				
	Mean phase stress	Al ₂ O ₃ (300)	Al ₂ O ₃ (116)	Al ₂ O ₃ (113)	Al ₂ O ₃ (006)
A-5YTZP (slip)	-75±12	-210±20	7±10	-107±15	175±15
A-5YTZP (tape)	-70±12	-205±20	7±12	-106±15	176±20
A-40YTZP (slip)	-315±13	-440±20	-260±20	-360±15	-118±17
A-40YTZP (tape)	-315±15	-440±20	-268±17	-363±17	-130±20

Table 5.7. The average residual stress values of selected peaks for Y-TZP phase, comparing it with the corresponding mean phase stresses, as previously reported in section 5.2.3.1.

Sample	$\sigma_{\text{Y-TZP}}$ (MPa)			
	Mean phase stress	Y-TZP (103)	Y-TZP (200)	Y-TZP (112)
A-5YTZP (slip)	740±40	2000±100	280±60	1160±70
A-5YTZP (tape)	720±40	1800±100	320±40	1120±50
A-40YTZP (slip)	370±20	1400±40	-120±20	720±20
A-40YTZP (tape)	360±40	1400±60	-130±40	700±30

5.2.4 Diffraction line broadening

Peak broadening was observed in the Y-TZP reflections in all investigated the A/Y-TZP composites during the Rietveld refinement of the TOF diffraction profiles.

However, for the Al_2O_3 matrix, the peak broadening can almost be ignored, especially in the A-5YTZP composites. Only slight peak broadening was detected in the Al_2O_3 in the A-40YTZP samples.

Taking the strongest peaks of the Al_2O_3 and Y-TZP phases from A-40YTZP(tape) sample, Al_2O_3 (113) and Y-TZP (112) (neighboring the Y-TZP (200)), as an illustration, the peak broadening behavior is exhibited in **Fig. 5.18**. The observed (measured) peak profile from diffraction scanning is shown as a blue line. If only the instrument effect is considered, which was precisely determined from the refinement of CeO_2 standard powder, peak fitting of Y-TZP (112) (neighboring the Y-TZP (200)) without physical broadening was relatively narrower than the measured peaks, as shown as a green line in **Fig. 5.18**. The corresponding difference curves (between the observed and the calculated profile) showed some fluctuations at the bottom of profiles, with $R_{\text{wp}}=15\%$. After introducing the sample physical effects of crystallite size and microstrain into the refinements, much better fitting (red line) was achieved, as can be judged from the flatter difference curves (black line), with $R_{\text{wp}}=6\%$. No obvious anisotropic broadening was observed in the profile fitting, indicating the absence of texture or preferred orientation in composites. From **Fig. 5.18** it is obvious that significant broadening was present in the Y-TZP peaks, but not in Al_2O_3 . It might be due to the relative larger grain size, as well as the relatively more isotropy lattice axial CTE, of the Al_2O_3 matrix than the Y-TZP in our materials.

Fig. 5.18. Peak broadening of Al_2O_3 (113), Y-TZP (112) (neighboring Y-TZP (200)) reflections from the A-40YTZP (tape) sample: observed (measured) peak profile in the neutron diffraction measurement, blue line; fitting without physical broadening, green line, with corresponding difference curve (between the measured and the calculated profile) as a light grey line, $\text{Rwp}=15\%$; fitting with broadening, in red line, with corresponding difference curve in black line, $\text{Rwp}=6\%$.
(a) Al_2O_3 (113) reflection; (b) Y-TZP (112) reflection (neighboring Y-TZP (200)).

Peak broadening analysis was conducted using the Rietveld method combined with the “Double-Voigt” modelling [31, 169]. Note that all the size and strain-related parameters were refined simultaneously in the final step of the Rietveld analysis.

It was discovered that size broadening was predominate in the Al_2O_3 phase in all of the A/Y-TZP composites, where strain-related parameters, both of its Gaussian and Lorentzian components, were refined to invalid values (very large error values). This negligible micro-strain behavior of alumina was also reported in [231] and it is consistent with a quasi-homogenous strain field in Al_2O_3 matrix.

For the Y-TZP phase, the peak broadening was mainly due to strain-broadening, in which Gaussian components were more pronounced than the Lorentzian ones, with a ratio of the Gaussian to the Lorentzian integral breadth (β_G / β_L) of strain-broadening in the 2~4 range. Size broadening effects were negligible. Strain-broadening is generally caused by the non-uniform displacements of the atoms with respect to their reference-lattice positions [171, 234]. In A/Y-TZP system, it was reported that atomic displacements were coupled to spontaneous strain during zirconia phase transition [235]. In this work, 30 vol.% *m*- ZrO_2 was transferred to *t*- ZrO_2 during sintering. Point defects associated to oxygen vacancies

were anticipated, as well as the induced inhomogeneous internal strain. In addition, the inhomogeneous distribution of yttria was observed during sintering in another work [231] with similar materials, inducing a defective core-shell structure of Y-TZP grains, which could also give rise to microstrain in the Y-TZP.

The volume-weighted domain sizes (D_V) of Al_2O_3 in A-40YTZP composites and maximum of microstrain (e) values of Y-TZP in A/Y-TZP composites were evaluated, as presented in **Fig. 5.19**. The data correspond to average values over different scanned positions in each bulk sample, with standard errors represented in error bars.

Fig. 5.19. Size-strain line-broadening results after the Rietveld refinement: the average volume-weighted domain sizes, D_V , of Al_2O_3 (the Y axis at right, in black) and maximum of microstrain, e , in Y-TZP in all of the studied A/Y-TZP composites (the Y axis on the left, in red). Note that the presented D_V and e were average values obtained over different measurement positions in each sample, with the standard errors represented in error bars.

As no obvious broadening was observed in the Al_2O_3 reflections in the A-5YTZP composites, the domain size D_V of the $\alpha\text{-Al}_2\text{O}_3$ crystal was only given in the A-40YTZP composites, which showed very similar values (around 150 nm) between the tape casting and the slip casting samples. Not much difference was found between the D_V values measured in the in-plane and the normal directions, indicating the spherical crystallite shape as well as homogenous size distribution in the Al_2O_3 . The broadening due to crystallite size is caused by the finite size

components diffracting incoherently with respect to one another [234]. However, above a certain crystallite size ($\sim 1\mu\text{m}$), this type of broadening is almost negligible in diffraction [236]. For the A-5YTZP composites, the average grain size of the Al_2O_3 matrix was generally higher than one micrometer, and consequently broadening behavior was hardly observed. As the Y-TZP content increased, grain growth of the Al_2O_3 matrix became inhibited, leading to appearance of several fine grains (shown in Fig. 4.1). Reduced crystal size was correspondingly anticipated, which explains the slight broadening phenomena in the Al_2O_3 peaks in the A-40YTZP composites. The determined domain size of the Al_2O_3 (around $0.15\mu\text{m}$) in the A-40YTZP samples was much smaller than the average grain size of Al_2O_3 ($1.0 \pm 0.2\mu\text{m}$) measured from SEM micrographs. This could be understood due to the domain size is not generally the same thing as the grain/particle size. Considering the suggested crystallite sizes ($<1\mu\text{m}$) for accurate evaluation using powder diffraction techniques, the reliability of obtained domain size D_V of the Al_2O_3 in real physical validity needs a careful assessment and confirmation by other supporting work like TEM (Transmission Electron Microscope).

As the Y-TZP vol. % increases, an increase in microstrain ϵ in the Y-TZP crystallite was detected, varying from around 4.6×10^{-4} in the A-5YTZP to 6.1×10^{-4} in the A-40YTZP composites. This increasing trend agrees well with the findings of Wang *et al.*[122] and A. Reyes-Rojas *et al.*[237], which previously reported a linearly increase in of microstrain with an increase in ZrO_2 % in the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ composites. In the work of A. Reyes-Rojas *et al.*[237], the values of the microstrain in the t- ZrO_2 phase were reported from 0.59 to 1.23 (10^{-3}) as the content of t- ZrO_2 increases from 5.5 wt. % to 11.5 wt. % in the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (1.5 mol% Y_2O_3) composites manufactured by hot isostatic pressing HIP (sintering at $1,575^\circ\text{C}$ and $1,600^\circ\text{C}$). As a comparison, the detected microstrain in present studied materials was definitely smaller, which might be due to many reasons (e.g. difference in the Y_2O_3 content, the sintering temperatures and manufacturing techniques). The increase in the microstrain ϵ in the Y-TZP crystallite indicates that the number of lattice defects is increased with the Y-TZP content.

No significant difference was detected in the microstrain of the Y-TZP due to the different manufacturing techniques (tape casting and slip casting). The slight difference between the A-5YTZP (slip) and the A-5YTZP (tape) was allowed considering the small addition of Y-TZP in composites and the consequently increased uncertainty in the analysis. Differences between the in-plane and the normal directions were not obvious and included in experiment error ranges for all composites.

5.3 Contribution of residual stresses to mechanical properties

According to the above residual stress measurements by both CW and TOF neutron diffraction techniques, it could be concluded that the residual stresses in present studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites were mainly induced by thermal and elastic mismatches between phases. Tensile stresses were developed in the Y-TZP particles and compressive ones were in the Al_2O_3 matrix, due to the thermal expansion mismatch between them. The scheme of thermal residual stress distribution in the A/Y-TZP composites was simply shown in **Fig. 5.20**.

Fig. 5.20. The scheme of thermal residual stress distribution in the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites.

Improvement in mechanical properties, e.g. flexure strength and fracture toughness, was observed with the addition of Y-TZP in the currently investigated A/Y-TZP composites, as reported in Chapter 4. Crack deflection, branching and bridging have been observed during the crack propagation and fracture process. It can be attributed to different mechanisms: (i) the t-m phase transformation [110, 238], (ii) crack deflection [239], (iii) microcracking [240] and (iv) the thermal residual stresses induced during the cooling stage of sintering by thermal and elastic mismatch between the particles and the matrix [193, 198]. As the first three have been extensively investigated by many research works, the contribution of residual stresses to the fracture toughness will be theoretically discussed in this work.

5.3.1 Residual stress & Crack deflection

According to the detailed mechanical studies of the A/Y-TZP composites in Chapter 4, crack deflection by the Y-TZP particles was observed in the indentation cracks in all of the composites studied (**Fig. 4.13** and **Fig. 4.14**). These phenomena are closely related to the localized residual stress fields which are developed as a result of phase transformation, thermal expansion mismatch or by the fracture of a second phase, as explained by Evans *et al.* [113-115]. The crack deflection could lead to a degree of toughening dictated by the reduced force on the deflected portion of the propagating crack [198]. Wei and Becher consider the thermal residual stress which is induced by the CTE mismatch as a major cause of crack deflection but they have made no quantitative estimate of the increased toughness.

Fig. 5.21 shows a schematic diagram of the crack deflection per particle (thermal expansion coefficient of particles greater than that of the matrix, $\alpha_p > \alpha_m$) and the associated residual stresses developed in the particle-reinforced composites, with radial tensile stress (σ_{rm}) and hoop compressive stress ($\sigma_{\theta m}$) generated [201, 241]. In this deflection model, the radial tensile stress (σ_{rm}) is taken as equal to the hydrostatic stress developed with the particle (σ_p) [201].

It is generally accepted that, during the crack propagation process under an external load, a crack will be expected to propagate in a direction parallel to the axis of the local compressive stress and perpendicular to the axis of the local tensile stress in the matrix surrounding the particle. If the particle is in the plane of the crack, the crack should be first deflected out of the plane as it approaches the particle, where the compressive hoop stress axis (in the matrix) is normal to the crack plane. As the crack moves around the particle and until the crack tip reaches the position above the particle, the orientation of crack is normal to the radial tensile stress, then it can be deflected back to the particle-matrix interface (**Fig. 5.21**). As regards the A/Y-TZP composites, with higher thermal expansion in Y-TZP particles ($\alpha_{\text{YTZP}, 25-1000^\circ\text{C}} = 10.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) than in the Al₂O₃ matrix ($\alpha_{\text{A}, 25-1000^\circ\text{C}} = 8.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), the crack is deflected away from the Y-TZP particles, resulting in the tortuous crack path, as shown in **Fig. 4.13** and **Fig. 4.14**.

Fig. 5.21. Schematic diagram of the deflection of the crack by particle (thermal expansion coefficient of particles greater than that of the matrix, $\alpha_p > \alpha_m$) and the associated residual stresses developed (radial tension and hoop compression) in particle-reinforced composites [201, 242]. Crack moving in plane of particle will the first to be deflected (compressive hoop stress axis (in the matrix) is normal to the crack plane). As the crack moves around the particle it can be attracted to the particle interface (normal to tensile radial stress axis (in the matrix)).

The averaged thermal residual stresses for both Al_2O_3 matrix and Y-TZP particulates in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites have been precisely determined by TOF neutron diffraction in section 5.2.3.1, as summarized in **Table 5.6** and **Table 5.7**. Taking the mean phase stresses as hydrostatic stresses for Y-TZP particulates and Al_2O_3 matrix, thus they are equal to the radial tensile stress (σ_{rm}) and hoop compressive stress ($\sigma_{\theta m}$) respectively. It's clear that with the increase of Y-TZP content in composites, the radial tensile stresses were decreased and the hoop compressive stress ($\sigma_{\theta m}$) were increased. It was proposed [242] that the residual hoop compressive stress developed in the A/Y-TZP ceramic composites accounts for the higher tendency of crack deflection, therefore for the enhancement of strength and fracture toughness. An increase in frequency of crack deflection was observed with the Y-TZP content in the A/Y-TZP composites, by comparing the SEM crack profiles of A-5YTZP (**Fig. 4.13 a**) and A-40YTZP (**Fig. 4.14 a**).

The crack-tip stress intensity can be altered by the crack deflection, and therefore increased toughness. For example, when the crack front is twisted out of the plane between two particles or the crack plane is tilted out of the plane normal to the applied stress axis, the matrix and the particles will locally experience mixed-

mode stress intensities, as discussed by Faber and Evan [113, 121]. It leads to a decrease in the mode I (pure tension) stress intensity acting on a deflected crack, consequently, increasing the macroscopic critical fracture toughness in mode I loading, K_{Ic} . The experimental works, by both the single edge laser-notch bending test and the indentation fracture test, have confirmed the above theories. It showed that with the increase in the Y-TZP second-phase content and consequently the greater frequency of crack deflection, the K_{Ic} of the A/Y-TZP composites were enhanced.

There are some models [113, 207, 228] proposed for quantitative estimation of fracture toughness due to the contribution of residual stresses in particulate-reinforced composites. In this work, the residual stresses in the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites have been precisely measured by neutron diffraction. It is possible to calculate the change in the mode I stress intensity factor, ΔK , and the behavior of the fracture toughness, K_{Ic} , due to the compressive residual stress in the matrix.

A simple model proposed by Taya *et al.* [228] was used for the calculation in this work, where the thermal residual stresses were postulated as a periodic tensile-compressive stress field, based on the framework of the Faber-Evans crack deflection model [113, 121] and Cutler and Vikar [243] toughening model.

Fig. 5.22. Semi-infinite crack advance through matrix compressive region[228].

Consider a semi-infinite crack surrounded by the particulate-reinforced composites with a thermal residual stress distribution. For the purpose of the fracture mechanics analysis, it can be approximated by an averaged uniform compressive

stress in the matrix, acting normal to the crack plane ahead of a semi-infinite crack, as shown in **Fig. 5.22**. Toughening by the local average compressive stress can be described as:

$$\Delta K_I = 2q\sqrt{\frac{2(D-d)}{\pi}} \quad (5.9)$$

where ΔK_I is the variation in the stress intensity factor, q is the local residual compressive stress, D is the interparticulate distance and d denotes the average diameter of the Y-TZP particles.

Due to the similar microstructure and fracture toughness between the tape casting and the slip casting samples with the same Y-TZP addition (chapter 4), the calculation of the variation in fracture toughness here was processed as a function of the Y-TZP content, irrespective of the fabrication methods. The parameters used in the calculation for both the A-5YTZP and the A-40YTZP composites were given below:

In the A-5YTZP composites: $q = \sigma_m = -75$ MPa, $D = 2$ μm , $d = 0.3$ μm

In the A-40YTZP composites: $q = \sigma_m = -315$ MPa, $D = 1$ μm , $d = 0.4$ μm

Here the average interparticulate spacing, D , was obtained from five SEM micrographs containing at least 100 Y-TZP particles.

The predicted decrease in the stress intensity factor by residual stresses was calculated as:

$$(\Delta K_I)_{\text{A-5YTZP}} = -0.156 \text{ MPa}\cdot\text{m}^{1/2} \text{ for A-5YTZP materials,}$$

$$(\Delta K_I)_{\text{A-40YTZP}} = -0.39 \text{ MPa}\cdot\text{m}^{1/2} \text{ for A-40YTZP materials.}$$

This reduction in ΔK_I is equivalent to an increase in the crack growth resistance by the same amount, denoted as $\Delta K_R = |\Delta K_I|$, which could be considered as the residual stress contribution to fracture toughness.

The above predicted increases in the fracture resistance could be compared with the ones measured in experiments. Taking the corresponding alumina matrix as the reference material with its reported $(K_{Ic})_A$ value of $\sim 3.8 \text{ MPa}\cdot\text{m}^{1/2}$ in the literature [185], as well as the average K_{Ic} measurement results of A/Y-TZP composites from single edge laser-notch bending test (**Table 4.5**), the experimental

increase in fracture toughness due to the addition of Y-TZP second phase was obtained following the equations below:

$$\Delta K_R = (K_{IC})_{\text{composites}} - (K_{IC})_A \quad (5.10)$$

The experimental increase of fracture toughness in the A-5YTZP composites is:

$$(\Delta K_R)_{A-5YTZP} = (K_{IC})_{A-5YTZP} - (K_{IC})_A = 4.4 \text{ MPa.m}^{1/2} - 3.8 \text{ MPa.m}^{1/2} = 0.6 \text{ MPa.m}^{1/2},$$

and that in the A-40YTZP composites is

$$(\Delta K_R)_{A-40YTZP} = (K_{IC})_{A-40YTZP} - (K_{IC})_A = 5.7 \text{ MPa.m}^{1/2} - 3.8 \text{ MPa.m}^{1/2} = 1.9 \text{ MPa.m}^{1/2}.$$

It is clear from the above that the increases in fracture toughness in experiments are much higher than the ones predicted by the crack deflection model which only considers the effect of residual stress. Thus, the crack deflection associated with residual stresses cannot fully account for the toughening of the Al₂O₃/Y-TZP composite. It means that other toughening mechanisms, like the $t \rightarrow m$ phase transformation, microcracking, etc., will be mainly responsible for the increased fracture toughness.

5.3.2 Residual stress & transformation toughening & microcracking

It is well accepted that the tensile residual stress will decrease the critical transformation stress and as a result crack tip transformation will occur at a much lower stress level [6]. Therefore, with the addition of Y-TZP into the alumina matrix, the development of tensile residual stress in the Y-TZP phase contributes additionally to the enhanced stress induced transformation of the retained tetragonal zirconia in the crack tip stress field. This corresponds well with the increased toughness achieved by the A/Y-TZP composites compared to the corresponding alumina matrices. However, with the increase in the Y-TZP volume fraction in the composites, the interaction opportunity between the crack tips and the transferable Y-TZP grains has increased but the tensile stresses in the Y-TZP phase have decreased. These offsetting effects make the influence of RS on both the transformation and microcracking toughening uncertain and hardly to be statistically analyzed.

5.4 Summary and conclusion

In this chapter, through-thickness residual strain measurement was carried out in the studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ bulk samples, by means of both constant-wavelength and time-of-flight neutron diffraction techniques. Stresses were precisely determined and combined with the appropriate analysis methods, e.g. the single peak fitting and the Rietveld refinement. The results obtained were compared to available data in the literature and to estimations by theoretical models. The effects of the Y-TZP content and green processing routes (the novel tape casting and conventional slip casting) were investigated. Combined with the mechanical properties in the currently studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials (Chapter 4), the contribution of residual stresses to toughening was discussed theoretically.

The main conclusions in this chapter are briefly summarized:

- 1) Due to the mismatch in the thermal expansion between the matrix and the particles, tensile residual stresses developed in the Y-TZP particulates and the compressive ones in the Al_2O_3 matrix. Almost flat through-thickness mean phase residual stress profiles were obtained in both phases. By increasing the Y-TZP content in the composites, a decrease in tensile stress in the Y-TZP phase and an increase in compressive stress (absolute values) in the Al_2O_3 matrix was found. The residual stress values obtained from neutron diffraction measurements are consistent with those reported in the literature as well as with the predictions of a modified Eshelby model.
- 2) Residual stresses varied along different hkl reflections for both the Al_2O_3 matrix and the Y-TZP particulates. Almost flat residual stress profiles through thickness were obtained for all of the selected individual reflections of both the Al_2O_3 and the Y-TZP phases. By increasing the Y-TZP content in composites, the absolute values of stresses in each selected reflections in the Al_2O_3 matrix they increased and in the Y-TZP phase they decreased, consistent with their mean phase stress behaviors.
- 3) Crystallite structures of both $\alpha\text{-Al}_2\text{O}_3$ and Y-TZP varied with the different Y-TZP addition in A/Y-TZP ceramics. The results obtained indicated that with a small addition of Y-TZP inclusion in the A/Y-TZP bulks, the predominant effect on the Al_2O_3 matrix was thermal expansion anisotropy and on the Y-TZP it was thermal expansion mismatch between phases. As the Y-TZP% increased, the dominating effects changed inversely.

- 4) Peak broadening in the Y-TZP reflections was observed in all investigated A/Y-TZP composites, but not in the Al_2O_3 reflections. The line-broadening of the Y-TZP peaks was mainly due to non-uniform micro-strains. By increasing the Y-TZP content in the A/Y-TZP composites, the non-uniform microstrain ϵ in the Y-TZP crystallite increased from around $4.6 (\times 10^{-4})$ in the A-5YTZP to $6.1 (\times 10^{-4})$ in the A-40YTZP composites.
- 5) No obvious difference in residual stresses and peak broadening was observed due to sample orientation (in-plane and normal directions) and the manufacturing processes (the novel tape casting and the conventional slip casting). A hydrostatic stress state was achieved and it was found that the novel tape casting process does not change the residual stresses state, which is mainly associated to thermal residual strains.
- 6) Crack deflection is considered to depend greatly on the effect of residual stress on the literature. A theoretical model for crack deflection was used. It showed that the crack deflection associated with the measured residual stresses cannot fully account for the increase in fracture toughness observed on the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composite. The residual stress state does not have a noticeable effect on the mechanical properties of alumina-zirconia composites. Consequently, other toughening mechanisms, like the tetragonal to monoclinic phase transformation, microcracking, etc., should also be considered.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

In this study, $\text{Al}_2\text{O}_3/\text{Y-TZP}$ particulate-reinforced composites consisting of 5 to 40 vol.% Y-TZP particulates were studied. A new tape casting route, which involved the stacking of green ceramic tapes at room temperature and using low pressures, was used for manufacture and compared with the conventional slip casting method, for the purpose of using it for the future production of laminated materials. The mechanical and fracture behavior and residual stresses were carefully investigated.

The following main conclusions have been drawn from this work:

- 1) Good microstructures, such as high density, the homogeneous dispersion of particles and grain size, defect-free interface, were obtained through the novel tape casting method for $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites. The inhibition effect was exhibited on the Al_2O_3 matrix grains with the addition of Y-TZP particulates. The tetragonal zirconia phase was almost fully retained in composites after final manufacture.

- 2) By increasing Y-TZP content in composites, the density of the materials, flexural strength and fracture toughness improved, while the hardness and elastic modulus decreased.
- 3) Residual stresses were determined for both the Al_2O_3 and the Y-TZP phases (mean phase stresses) as well as for individual reflections of both phase (peak-specific residual stresses), by means of constant-wavelength and time-of-flight neutron diffraction techniques. As regards the mean phase stresses, tensile residual stresses were developed in the Y-TZP particulates and the compressive ones in the Al_2O_3 matrix. Peak-specific residual stresses showed a remarkable variation for different hkl reflections for both phases. Almost flat through-thickness stress profiles were obtained in the A/Y-TZP bulk samples, for both the mean phase residual stresses as well as the peak-specific residual stresses. By increasing the Y-TZP content in the composites, the absolute values of the stresses in the Al_2O_3 matrix increased and in the Y-TZP phase they decreased, irrespective of the mean phase stresses and peak-specific residual stresses.
- 4) Crystallite structures of both $\alpha\text{-Al}_2\text{O}_3$ and Y-TZP were determined by the Rietveld analysis, which varied with a different Y-TZP addition in the A/Y-TZP ceramics.
- 5) Peak broadening in the Y-TZP reflections was observed in all investigated A/Y-TZP composites, mainly due to the non-uniform micro-strain in crystal. The determined microstrain ϵ in the Y-TZP crystallite was increased with the the Y-TZP content in composites. The line broadening phenomena was almost negligible in the Al_2O_3 reflections.
- 6) No obvious sample orientation effect was observed, according to the microstructure, residual stresses and peak broadening in both the in-plane and normal directions in samples.
- 7) Various fracture modes were observed in fractured A/Y-TZP samples, of which the predominant one varied with the Y-TZP content. The possible toughening mechanisms were discussed, e.g. the stress-induced transformation toughening, transformation-induced microcracking, as well as the internal residual stresses.
- 8) Residual stresses are usually considered to have an influence on the mechanical properties of ceramic composites, although residual stress profiles are rarely measured in these materials. In this work, the residual stress states in Al_2O_3 /Y-TZP composites were precisely determined by means of non-destructive

measurements—neutron diffraction. The contribution of residual stresses to the fracture toughness of ceramic composites was also investigated by using theoretical models. It was found that the increase in fracture toughness predicted by the models is much smaller than the one observed experimentally. Consequently, in this case residual stresses do not seem to be the main factor responsible of toughening due to the addition of zirconia.

- 9) No significant effects were induced by the different manufacturing processes (the novel tape casting and conventional slip casting), in terms of microstructure, mechanical performance and residual stresses in the A/Y-TZP ceramics studied. It showed that the quality of the ceramics manufactured using the novel tape casting method was assured (e.g. defect-free interface between the individual tapes, homogeneities in the microstructure, high mechanical performance, etc.), indicating that it could be a promising candidate for laminated ceramics manufacture in the future.

6.2 Future work

In the author's opinion, future investigations can be conducted in the following aspects:

- i) The wear application is one of the most interesting fields for investigation. Tribological behavior under several wear conditions (friction velocities, loads and environments) can be studied, and related to the influence of residual stresses.
- ii) Application of the new tape casting routes to the preparation of laminated $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials, with different tape thickness, tape composition and tape stacking sequence, etc., as well as its mechanical characterization.
- iii) In-situ residual stress measurements under applied load should be investigated, to access the behavior of different reflections in a more detailed way. In addition, residual stress measurements should be performed at high temperatures, in order to study their relaxation.
- iv) The transformation from tetragonal to monoclinic zirconia could be investigated by performing neutron diffraction experiments in-situ, while applying load to a notched sample. The fracture process zone at the crack tip could be imaged to see how the transformation proceeds.

- v) The mechanical and fracture behavior as well as residual stresses at high temperatures could be investigated. The stress behavior of different reflections at high temperature could be accessed.

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List of Figures

Fig. 2.1. Categorization of residual stresses according to length scales in a two-phase material.....	7
Fig. 2.2. Conventional monochromatic two theta scanning at a constant flux source.	13
Fig. 2.3. Schematic of a typical pulsed source based time-of-flight instrument for strain measurement.....	14
Fig. 2.4. Schematic indicative of the approximate current capabilities of the various techniques for residual stresses measurement.	15
Fig. 2.5. Schematic illustration of Bragg scattering.	16
Fig. 2.6. Diffraction peak profile for (a) zero strain (no macrostrain and no microstrain), (b) (compressive) macrostrain and/or type II strain, (c) microstrain. .	17
Fig. 2.7. Stress and strain components in the direction of the scattering vector given by the tilt angles (ψ, ϕ) at a measurement point (x, y, z) in the specimen co-ordinate system.	18
Fig. 2.8. Schematic representation of phase transformations between the three polymorphs of ZrO_2 and their corresponding space groups: (a) cubic ($Fm\bar{3}m$), (b) tetragonal ($P4_2/nmc$), and (c) monoclinic ($P2_1/c$).[65].....	26

Fig. 2.9. The phase diagram of $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system at 1450 °C	28
Fig. 2.10. Schematic showing the stress-induced phase transformation of metastable tetragonal zirconia particles in the crack tip stress field.....	32
Fig. 2.11. Microcrack toughening induced in the zirconia ceramics as a result of the formation and the subsequent growth of microcracks, as a consequence of stress-induced t- ZrO_2 phase transformation in the process zone.	33
Fig. 3.1. XRD analysis of the raw powders used for $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites..	38
Fig. 3.2. Schematic arrangement of sample in a three-point bend test..	43
Fig. 3.3. View of the sharp Laser-V-notch on the investigated specimens.	46
Fig. 3.4. Experiment set-up in the single edge laser-notch beam (SELNB) test.	47
Fig. 3.5. Schematic arrangement of laser-notched beam sample in SELNB test.	47
Fig. 3.6. Top and cross-sectional views of the crack formation through Vickers indentation. (a) the Palmqvist crack model and (b) the half-penny/Median crack model.	49
Fig. 3.7. Schematic illustration of indentation load–displacement data showing important measured parameters.....	51
Fig. 3.8. Overview picture of the SALSA strain scanning instrument at the ILL, Grenoble.....	54
Fig. 3.9. Experimental set-up of residual stresses measurement by constant-wavelength neutron diffraction in SALSA diffractometer, both in the (a) in-plane and (b) normal directions.	55
Fig. 3.10. Experimental set-up on the time-of-flight neutron strain scanner ENGINE-X at ISIS.....	57
Fig. 3.11. The TOF neutron diffraction patterns of the standard CeO_2 powder (blue line), as well as its fitting profiles (red line) by Rietveld refinement..	61
Fig. 4.1. SEM micrographs of polished and chemical etched surfaces of the studied materials.	71

Fig. 4.2. X-Ray diffraction profiles of the sintered $\text{Al}_2\text{O}_3/\text{Y-TZP}$ (tape casting) composites.	72
Fig. 4.3. The linear section of stress-strain curves for determination of the elastic modulus, obtained by means of three-point bending tests.....	74
Fig. 4.4. Scheme of the Vickers indentation at the polished cross section of the sintered A/Y-TZP samples. (a) Indentation performed in the interface zone ($\diamond$) and in the constituent tapes ($\blacklozenge$). (b) scheme of top view of the indentation imprints and cracks formed.	75
Fig. 4.5. The typical top view of Vickers indentation imprints and cracks in A/Y-TZP composites.	77
Fig. 4.6. Experimental apparent stress–strain curves in three-point bending test on the investigated $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites.....	78
Fig. 4.7. Representative load-displacement curve recorded during the single edge laser-notch beam (SELNB) bending tests.....	79
Fig. 4.8. The fracture surfaces of studied $\text{Al}_2\text{O}_3/\text{Y-TZP}$ materials at low magnification.....	82
Fig. 4.9. The represent view of fracture part near the notch edge in A-40YTZP (tape) composites, without regular semi-elliptical surface cracks.....	83
Fig. 4.10. Scanning electron micrographs of the fracture surfaces of $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites.	85
Fig. 4.11. The evolution of indented surface view in A-5YTZP composites (for both tape casting and slip casting samples).....	88
Fig. 4.12. The evolution of indented surface view in A-40YTZP composites (for both tape casting and slip casting samples).....	89
Fig. 4.13. Typical indentation crack profiles in A-5YTZP composites, representing both tape casting and slip casting samples.....	91
Fig. 4.14. Typical indentation crack profiles in A-40YTZP composites, representing both tape casting and slip casting samples.....	92

Fig. 4.15. The typical SEM micrographs of 1500 nm penetration depth nanoindentation imprint on A-5YTZP(tape) materials.	95
Fig. 4.16. The representative indentation load (P)-displacement (h) curves of each A/Y-TZP composites.	95
Fig. 4.17. The elastic modulus (E) vs displacement (h) curves for all the A/Y-TZP materials investigated.	96
Fig. 4.18. Hardness (H) vs displacement (h) curves for all the A/Y-TZP materials investigated.	96
Fig. 5.1. The measured and fitted CW diffraction patterns of Al_2O_3 (116) and Al_2O_3 (300) for Al_2O_3 starting powder.	105
Fig. 5.2. The measured and fitted CW diffraction patterns of YTZP (211) and YTZP (103) for Y-TZP starting powder.	105
Fig. 5.3. A 3D contour of the combine of through-thickness scanning profiles of Al_2O_3 (116) peak in A-5YTZP (slip) sample.	106
Fig. 5.4. The representative diffraction patterns of selected reflections of the Al_2O_3 and YTZP phases in A-5YTZP composites, regardless of the direction (in-plane and normal) and manufacturing techniques (tape casting and slip casting).	107
Fig. 5.5. The representative diffraction patterns of selected reflections of Al_2O_3 and YTZP phases in A-40YTZP composites, regardless of the direction (in-plane and normal) and manufacturing techniques (tape casting and slip casting).	108
Fig. 5.6. Through-thickness residual strain profiles in A-5YTZP and A-40YTZP composites manufactured by the conventional slip casting, both in the in-plane and normal directions.	111
Fig. 5.7. Through-thickness residual strain profiles in A-5YTZP and A-40YTZP composites manufactured by the novel tape casting technique, both in the in-plane and normal directions.	112
Fig. 5.8. Through-thickness residual stress profiles in Al_2O_3 /Y-TZP composites manufactured by the conventional slip casting technique, reinforced with 5 and 40 vol.% Y-TZP, both in the in-plane and normal directions.	113

Fig. 5.9. Through-thickness residual stress profiles in $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites manufactured by the novel tape casting technique, reinforced with 5 and 40 vol.% Y-TZP, both in the in-plane and normal directions.	114
Fig. 5.10. The TOF neutron diffraction patterns of Al_2O_3 starting powders (blue line), as well as its fitting profiles (red line) by Rietveld refinement.	118
Fig. 5.11. The time-of-flight neutron diffraction patterns with Rietveld refinement for Y-TZP starting powders.	119
Fig. 5.12. The representative TOF neutron diffraction patterns with Rietveld refinement for A-5YTZP (slip) samples.	121
Fig. 5.13. The representative TOF neutron diffraction patterns with Rietveld refinement for A-40YTZP (tape) samples.	122
Fig. 5.14. Mean phase stress profiles for Al_2O_3 (Δ) and Y-TZP ($\square$) phase along the thickness of A/Y-TZP (slip casting) bulk samples, both in the in-plane and normal directions.	128
Fig. 5.15. Mean phase stress profiles for Al_2O_3 (Δ) and Y-TZP ($\square$) phase through the thickness of A/Y-TZP (tape casting) bulk samples, both in the in-plane and normal directions.	129
Fig. 5.16. The through thickness residual stresses behaviors of Al_2O_3 (300), (116), (113), (006) in A/YTZP composites, measured in both in-plane and normal directions.	133
Fig. 5.17. The through thickness residual stresses behaviors of Y-TZP (103), (200), (112) in A/YTZP composites, measured in both in-plane and normal directions. ..	135
Fig. 5.18. Peak broadening of Al_2O_3 (113), Y-TZP (112) (neighboring Y-TZP (200)) reflections from the A-40YTZP (tape) sample.	139
Fig. 5.19. Size-strain line-broadening results after the Rietveld refinement: the average volume-weighted domain sizes, D_v , of Al_2O_3 (the Y axis at right, in black) and maximum of microstrain, e , in Y-TZP in all of the studied A/Y-TZP composites (the Y axis on the left, in red).	140
Fig. 5.20. The scheme of thermal residual stress distribution in the $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites.	142

Fig. 5.21. Schematic diagram of the deflection of the crack by particle (thermal expansion coefficient of particles greater than that of the matrix, $\alpha_p > \alpha_m$) and the associated residual stresses developed (radial tension and hoop compression) in particle-reinforced composites.. 144

Fig. 5.22. Semi-infinite crack advance through matrix compressive region. 145

List of Tables

Table 2.1. Criteria-of-fit in Rietveld refinement	24
Table 2.2. The overview of properties of alumina and Y-TZP materials.....	27
Table 3.1. The properties of raw powders used for $\text{Al}_2\text{O}_3/\text{Y-TZP}$ composites	38
Table 3.2. Selected formulas used for calculation of indentation fracture toughness.	49
Table 3.3. Initial crystal structure parameters used in refinement for A/Y-TZP materials system.....	62
Table 3.4. The bulk elastic constants used for the residual stresses calculation for A/Y-TZP materials systems.....	64
Table 4.1. Values of measured density (ρ), relative density (ρ_{relative}) and average grain size (G) in A/Y-TZP composites investigated.....	70
Table 4.2. The determined values of dynamic Young's modulus (E_{dyn}), shear modulus and Poisson's ratio (ν) by dynamic test and static Young's modulus (E_{flex}) by three-point bending test.....	73
Table 4.3. Sizes of Vickers indentation cracks and imprints at the cross sections of sintered A/Y-TZP pieces, as well as the Vickers hardness H_V	76

Table 4.4. The average values of flexure strength, σ_f , determined by three-point bending test.	78
Table 4.5. The fracture toughness K_{IC} of the studied A/Y-TZP composites obtained by Single Edge Laser-Notch Beam (SELNB) method.	80
Table 4.6. The fracture toughness K_{IC} of the studied A/Y-TZP composites obtained by the indentation fracture (IF) method using different equations.	87
Table 4.7. The average elastic modulus (E) and hardness (H) of A/Y-TZP composites obtained by nanoindentation.	98
Table 4.8. The main properties determined for the monolithic Al_2O_3 /Y-TZP composites.	101
Table 5.1. The stress-free peak information of the selected hkl reflections in Al_2O_3 /Y-TZP materials system, obtained from Al_2O_3 powder and Y-TZP powder data: peak position, 2θ , and stress-free lattice spacing, d_0^{hkl}	105
Table 5.2. The peak information of the studied reflections of the Al_2O_3 phase in Al_2O_3 /Y-TZP composites: peak position 2θ , d-spacing d_{hkl} , peak intensity and the peak width FWHM.	109
Table 5.3. The peak information of the studied reflections of the Y-TZP phase in Al_2O_3 /Y-TZP composites: peak position 2θ , d-spacing d_{hkl} , peak intensity and the peak width FWHM.	110
Table 5.4. The diffraction elastic constants (DEC) values used for residual stress calculation in CW neutron diffraction measurement.	112
Table 5.5. The unit-cell parameters ($\text{\AA}$) of α - Al_2O_3 phase and Y-TZP phase obtained from Rietveld refinement of starting powders and A/Y-TZP bulk composites (average values over different scanning points in each sample)	124
Table 5.6. The average residual stress values of selected peaks for Al_2O_3 phase, comparing it with the corresponding mean phase stresses, as previously reported in section 5.2.3.1.	137
Table 5.7. The average residual stress values of selected peaks for Y-TZP phase, comparing it with the corresponding mean phase stresses, as previously reported in section 5.2.3.1.	137