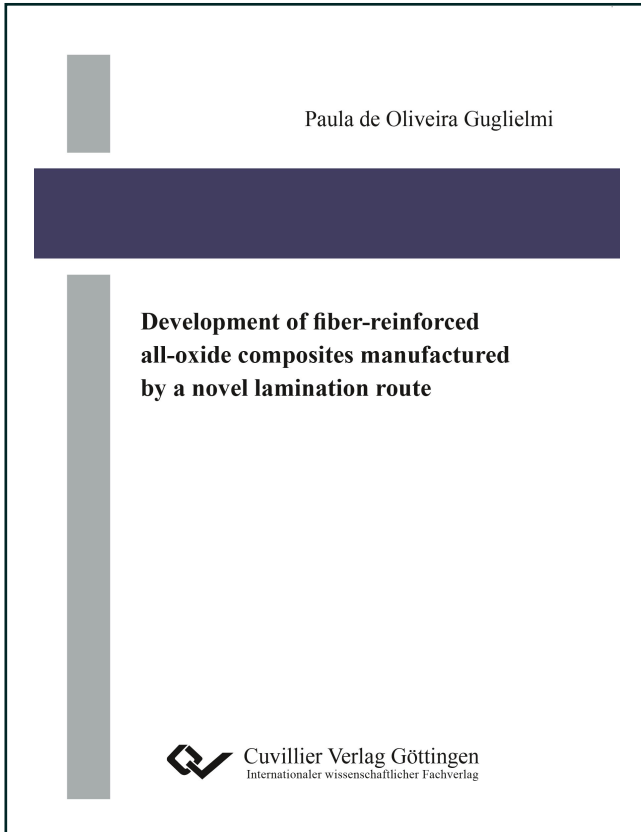




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**Development of fiber-reinforced all-oxide composites
manufactured by a novel lamination route**



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1 Introduction and Motivation

Overcoming the brittleness of ceramics is still a relevant topic in materials science. Extensive research effort has been dedicated to develop microstructural designs that enhance the toughness of these materials. One of the most effective approaches is the incorporation of continuous ceramic fibers as reinforcement [1]. Provided the fiber-matrix interfaces are weak, toughening mechanisms such as crack deflection, crack bridging and fiber pullout take place, yielding a quasi-ductile fracture behavior to the so-called ceramic matrix composite (CMCs) [1,2].

Among the different classes of CMCs, much attention has been drawn to all-oxide systems because of their chemical stability in oxidizing environments [3,4]. Toughness is typically achieved in these materials by a weak, porous matrix that enables debonding at fiber-matrix interfaces [3,5]. These composites are usually produced by liquid infiltration techniques, in which matrix particles are impregnated into fiber tows or fabrics via aqueous slurries or sols [3,6–8] and then sintered for consolidation. One of the challenges of this process is the consolidation of flawless matrices, since the constrained shrinkage imposed by the rigid network of fibers causes the formation of matrix cracks during drying and sintering [1,3]. Such cracks may not just be detrimental to the mechanical properties of the composite [8–10], but also compromise its thermal shock resistance by decreasing the thermal conductivity of the material [11,12]. A method to mitigate the formation of these cracks is therefore of great interest.

In order to produce crack-free CMCs, matrix shrinkage must be avoided in both drying and sintering steps [10]. When conventional liquid infiltration routes are used to produce composites reinforced with woven fabrics, drying cracks form during the extraction of the liquid carrier, mainly in matrix-rich regions located at the crossover between fiber tows [6,7]. Alternatives to mitigate these drying cracks were proposed by Levi *et al.* [7] and Yang *et al.* [13] and consist in reducing the amount of unreinforced matrix regions by filling the large inter-tow spaces with chopped fibers or large particles, respectively. Another possible



method was proposed by Mah *et al.* [10] and consists of a shrinkage-free freeze casting of camphene-based slurries used to infiltrate fiber fabrics or preforms. Although promising results were obtained by these methods, the viability of using them to produce all-oxide CMCs in large scales should yet be proved.

With regard to the sintering-related cracks, they can be avoided by using reactive sintering routes, which ideally reduce sintering shrinkages to zero [14]. Reaction bonded aluminum oxide (RBAO) arises here as a promising matrix material for all-oxide CMCs. The sintering shrinkage of RBAO ceramics can be partially or totally compensated by the expansion associated with the oxidation of Al particles, present in the precursor powders, during heat treatments in air [15,16]. Nevertheless, although often suggested in the literature as a promising matrix material [3,17,18], there is to date no report of the use of RBAO in the production of full-scale, all-oxide composites. Research in this area is restricted to the analysis of model and mini composites consisting of a few fibers or tows dispersed in the matrix [17–19]. Therefore, the benefits and possible drawbacks of using RBAO to produce all-oxide CMCs and the related effects on the final material properties are still unclear.

This work aims at investigating the viability of using RBAO to produce all-oxide CMCs with a reduced amount of shrinkage-related cracks. Due to the high reactivity of aluminum particles with water, conventional aqueous slurries cannot be used in the processing [16]. A novel manufacturing route is therefore developed, in which organic particle carriers are used. In this route, fiber woven fabrics are first infiltrated with a low viscous ethanol-based slurry for the impregnation of matrix particles within the fiber bundles. In a subsequent step, the large inter-tow voids are filled with a paraffin-based suspension used for the lamination of thermoplastic prepregs. This two-step impregnation route allows for an enhanced filling of void spaces within the fiber fabrics and guarantees a homogenous distribution of matrix particles throughout the green composites. Thereby, shrinkage is reduced and cracks are avoided also in the green state. Composites with both RBAO and a reference, all-oxide matrix are produced and characterized. A detailed analysis of the microstructure and mechanical properties of the produced composites allows for a critical evaluation of the developed processing route, as well as of the use of RBAO matrix in all-oxide CMCs.



1.1 Outline of the thesis

This thesis is divided into eight chapters. Chapters 1 and 2 comprise, respectively, this introduction and a literature review of relevant topics related to this work. Chapters 3 to 7 present the methodology used to achieve the objectives of this work, as well as the obtained results. Each of these chapters can be understood as a sub-project and can, in principle, be read separately. This structure improves the readability and comprehension of this thesis, since the methods used in each chapter differ from one another.

Chapter 3 presents preliminary studies performed on RBAO-matrix model composites, in order to determine suitable thermal treatment parameters for such composites. The knowledge acquired in this chapter is used later in the production of full-scale, all-oxide composites by the novel processing route developed in this work. Part of the experiments presented in this chapter were performed with the help of M.Sc. Seyed M. Goushegir, during his master thesis [20]. Valuable inputs to the theoretical model used in this chapter to evaluate the experimental data were given by M.Sc. João G. P. da Silva during his interchange at the Institute of Advanced Ceramics at TUHH.

In Chapter 4, the development of the novel processing route is presented, which is carried out using conventional, pure oxide matrix materials. The introduction of RBAO matrices in the composites requires other development steps, which are presented in Chapter 6. Part of the experiments presented in these chapters were performed with the help of Eng. Murilo P. Hablitzel, during his bachelor thesis [21].

Chapter 5 shows the microstructural characterization of reference composites produced with a pure oxide matrix consisting of 80 vol% Al_2O_3 and 20 vol% tetragonal ZrO_2 (A8Z2 matrix). This is the same composition as that of RBAO after the complete oxidation of the aluminum particles. Apart from being a reference material, these composites serve to evaluate the novel developed processing route. Finally, the mechanical properties of the different composites produced in this work are presented in Chapter 7, which is followed by a summary in Chapter 8.





2 Literature review

2.1 Ceramic matrix composites

Despite attractive properties such as temperature stability, high strength, low density, and good corrosion and erosion resistance, the inherent brittleness of ceramics still prevents their use in many structural applications. This drawback fostered the development of several microstructural designs to increase toughness and damage tolerance of these brittle materials. Microcracking, transformation toughening and reinforcement with particles, whiskers or continuous fibers are some examples of these designs [1,3,22], being the latter suggested as the most promising [1].

Long fiber reinforced CMCs present higher temperature capability than metals and intermetallics and larger strain to failure than monolithic ceramics [23,24]. Their mechanical behavior is normally referred to as *quasi-ductile*, even though all components (matrix, fibers and interphases) are brittle. These features, combined with their low density and corrosion resistance, make CMCs interesting for thermomechanical applications where weight saving, extended lifetime of components and elevated operating temperatures are desirable [4,25].

However, CMCs are a relatively new class of structural materials, being their use still limited to some niche applications in the aerospace and military industries, such as thermal protection [3,26] and engine nozzles [26,27], as well as brake systems for aircrafts and sport cars [27,28]. Nevertheless, the demand on high temperature materials for power generation systems, such as jet engines and stationary turbines, continues driving the interest of researchers and engineers in further developing and understanding these materials [4].

Since the early developments of fiber reinforced CMCs in the 1970s [29,30], much attention has been given to non-oxide systems composed of carbon or silicon carbide fibers, reinforcing a carbon or silicon carbide matrix [28,31,32]. The interest in these materials is explained by the high strength presented by the



covalent-bonded, non-oxide fibers at high temperatures and, most especially, by their excellent creep resistance [3,25]. However, non-oxide CMCs are prone to oxidation, which considerably limits their lifetime during applications in oxidative atmospheres [1,32,33]. This fundamental drawback has arisen the interest in developing composites consisting entirely of oxides [1,3,4,23]. The so-called all-oxide CMCs are the focus of the present work. A better overview on the developments in this area over the last decades is given in section 2.2. The following sections are dedicated to the mechanical behavior and toughening mechanisms associated with the reinforcement of ceramics.

2.1.1 Predictions of composite strength by the rule of mixtures

A fundamental difference between CMCs and other composite materials is that, in the former, both matrix and fibers are brittle. Unlike metallic or polymeric matrices, ceramic matrices are neither compliant nor ductile and cannot deform plastically prior to fracture [30]. Additionally, CMCs are considered inverse composites, since the failure strain of the matrix is lower than that of the fibers [34], as schematically shown in the stress-strain diagram in Figure 1(a). Consequently, the matrix is the first component to fail when a CMC is loaded.

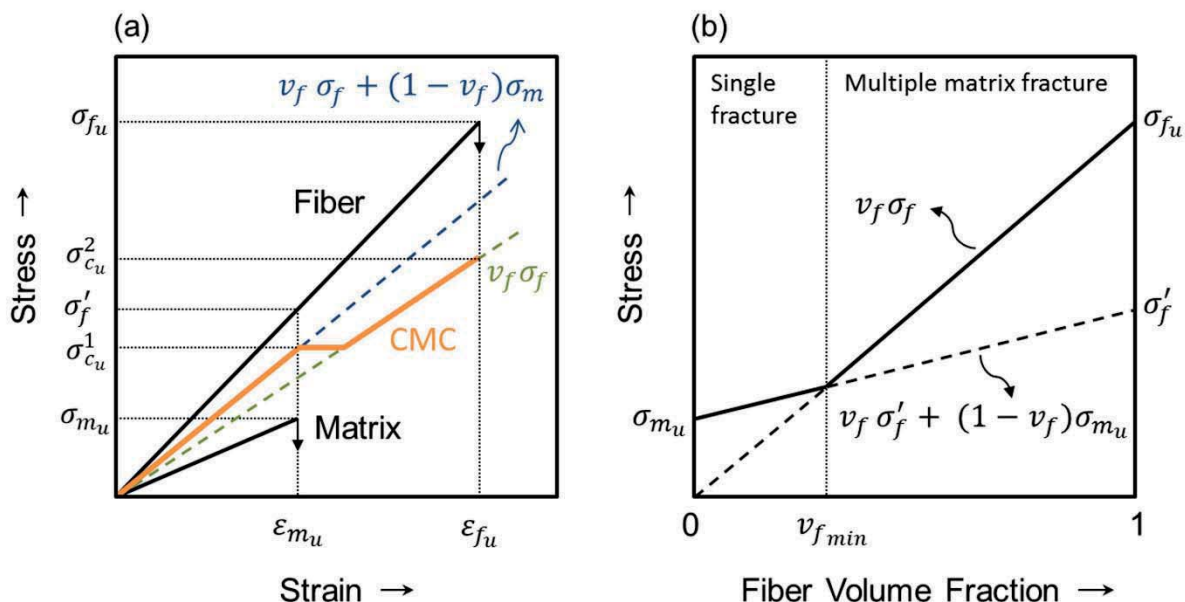


Figure 1: Schematic diagrams of an idealized ceramic matrix composite (CMC): (a) Stress-strain relationships of fiber, matrix and composite; (b) Dependence of composite failure stress on the fiber volume fraction. Adapted from Chawla [1] and Hull and Clyne [35].

Based on the mechanical properties of the fibers and the matrix and considering the volume fractions of both components, the mechanical behavior of the composite under axial tensile loading can be predicted by the rule of mixtures, as schematically shown in Figure 1. For that, it is assumed that the continuous fibers are parallel, unidirectional and homogeneously distributed in the matrix, besides presenting identical diameter and mechanical strength.

Before matrix cracking, i.e., for strains up to the failure strain of the matrix, ε_{m_u} , fibers and matrix are equally strained and the stress on the composite under axial loading, σ_c , can be calculated as follows [1,35]:

$$\sigma_c = v_f \sigma_f + (1 - v_f) \sigma_m \quad \text{Eq. 1}$$

where v_f is the volume fraction of fibers in the composite and σ_f and σ_m are the stresses on the fibers and the matrix at a given strain, respectively.

When ε_{m_u} is achieved, cracks start propagating in the matrix. Two situations may happen beyond this point: (i) if the fibers fail before the load is completely transferred from the matrix to them, then the ultimate tensile strength of the composite, $\sigma_{c_u}^1$, is a weighted average of the failure stress of the matrix, σ_{m_u} , and the stress applied to the fibers at the onset of matrix cracking, σ_f' [35]:

$$\sigma_{c_u}^1 = v_f \sigma_f' + (1 - v_f) \sigma_{m_u} \quad \text{Eq. 2}$$

If otherwise (ii) matrix cracks do not lead to the premature failure of the fibers, then a knee appears in the stress-strain curve, as schematically shown in Figure 1(a). Load is then progressively transferred from the matrix to the intact fibers, until it is completely carried by the reinforcement. In this case, failure occurs when the strain reaches the failure strain of the fibers, ε_{f_u} , and the ultimate tensile strength of the composite, $\sigma_{c_u}^2$, is simply given by [35]:

$$\sigma_{c_u}^2 = v_f \sigma_{f_u} \quad \text{Eq. 3}$$

where σ_{f_u} is the fiber ultimate tensile strength. The fact that the mechanical strength of the composite is, in this case, controlled by the fibers does not deplete the importance of having a matrix in the composite. Composite matrices are necessary, for instance, to ensure material integrity, to protect the fibers, to give a



shape to fiber-reinforced components, to guarantee cohesion in the transverse direction and for load transfer between matrix and fibers.

The situation described by Eq. 3 is only possible if the amount of fibers in the composite is enough to fully sustain the additional load, which was being carried by the matrix prior to its fracture. The minimum fiber volume fraction $v_{f_{min}}$ necessary for this to happen is determined by setting Eq. 2 equal to Eq. 3, resulting in [1,35]:

$$v_{f_{min}} = \frac{\sigma_{m_u}}{\sigma_{f_u} - \sigma'_f + \sigma_{m_u}} \quad \text{Eq. 4}$$

The dependence of composite strength on the fiber volume fraction is depicted in Figure 1(b). This figure allows for the following conclusions: (i) since $\sigma_{m_u} < \sigma'_f$, ceramic fibers will always lead to an increase in the CMC strength, being the benefit more pronounced when $v_f > v_{f_{min}}$, and (ii) the higher the fiber volume fraction, the higher the strength of the composite. In addition, according to Chawla [1], if $v_f > v_{f_{min}}$, a multiple crack failure occurs (non-brittle behavior), while for $v_f < v_{f_{min}}$, a single crack dominates the failure of the material (brittle behavior).

Although this treatment offers a good estimation of the composite strength under tensile load, it significantly simplifies the reality [1,35]. For instance, after the onset of microcracking, the slope of the stress-strain curve does not fall to zero. Instead, it changes gradually due to load transfer across the fiber-matrix interfaces [35,36]. Additionally, fibers follow a statistical Weibull distribution and do not present a single strength value, as assumed here. Moreover, a very important aspect of CMCs is not being considered in this analysis: the role of the fiber-matrix interfaces in the mechanical response of these materials.

In order for the fibers to be able to carry load after matrix failure, not just v_f must be greater than $v_{f_{min}}$, but also the fibers should remain intact, even though cracks are propagating in the matrix. For this to happen, matrix cracks must be either arrested or deflected at the fiber-matrix interfaces [33,34]. In CMCs, if the bonding between matrix and fibers is very strong, matrix cracks induce fiber fracture by a notch effect, even if $v_f > v_{f_{min}}$ [34]. In this case, the strength of the composite is most likely given by Eq. 2 and the material undergoes brittle failure. Otherwise, if the fiber-matrix bonding is weak enough, matrix cracks by-pass the fibers and

leave them intact and capable of carrying load [1,34]. In this case, composite strength is dominated by Eq. 3 and failure is accompanied by a series of energy absorbing mechanisms, such as matrix microcracking, debonding at fiber-matrix interface, crack bridging and fiber pullout.

Therefore, the reinforcement of a ceramic material with continuous fibers may not just increase its strength, but also, and frequently more important, may increase toughness and favor a non-catastrophic fracture of the material [1,30]. Hence, in order to design a CMC with enhanced mechanical properties, not just the fiber volume fraction should be optimized but, most essential, the interface between fibers and matrices.

Interfaces in CMCs have two important functions: (i) promote the deflection of matrix cracks and (ii) enable load transfer between matrix and fibers [34]. The first is crucial to achieve both strength and toughness, since both properties require that fibers are preserved from the damage of the matrix. The latter must be effective, so that high strength values are achieved [2,34]. On the one hand, crack deflection requires weak interfaces. On the other hand, load transfer is favored by fairly strong ones [34]. The design of effective interfaces for CMCs is therefore very challenging. They should be weak to promote crack deflection, but not too weak, so as to deplete load transfer. They should be strong to promote a good load transfer, but not too strong, so that fibers are prematurely broken, leading to the brittle failure of the composite. However, load transfer issues are usually disregarded and researchers focus mainly on the development of weak interfaces for crack deflection [2].

2.1.2 Microstructural designs for damage tolerance in CMCs

The different microstructural concepts to achieve crack deflection in CMCs are depicted in Figure 2. The most common concept is the introduction of a *weak interphase* between matrix and fibers (Figure 2(a)). This is achieved either by an *in-situ* chemical reaction during processing, or by coating the fibers prior to composite manufacturing [34,37]. This approach has been extensively used in non-oxide composites, mainly using C (carbon) or BN (boron nitride) interphases [34]. The disadvantage of these coatings is their susceptibility to oxidation, which normally leads to the embrittlement of the material [37]. If the interphase is



volatilized by oxidation, matrix and fibers may react and form a strong bonding that no longer allows the deflection of matrix cracks [4,38].

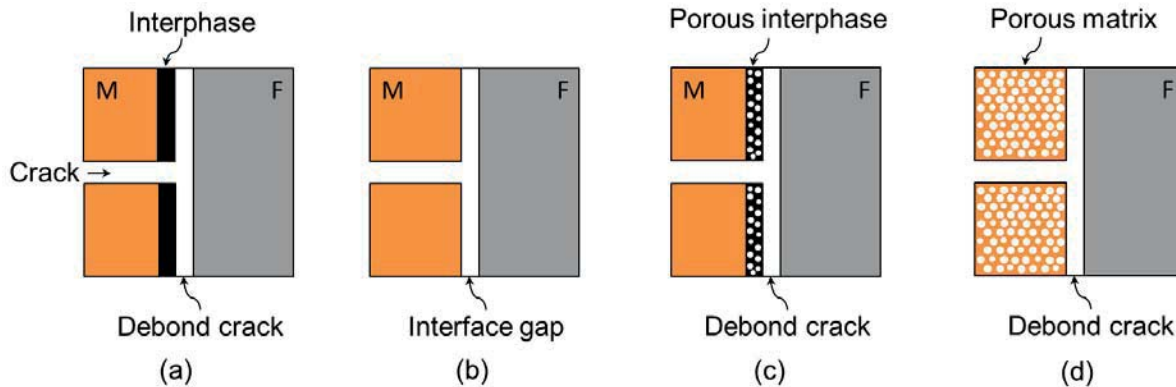


Figure 2: Microstructural designs for damage tolerance in CMCs: (a) weak interphase; (b) fugitive coating; (c) porous interphase; (d) porous matrix. M and F indicate the matrix and fiber, respectively. Adapted from Zok [4].

For all-oxide composites, La-monazite (LaPO_4) interphases show good results in terms of crack deflection, since this rare-earth phosphate bonds weakly to oxides and leads to low-toughness interfaces [4,23]. A drawback of this coating is the strength degradation caused on the oxide fibers due to deleterious reactions with monazite precursors during the necessary heat treatments [4,39].

Another way of controlling the interface properties in CMCs is through *fugitive coatings* (Figure 2(b)). In this concept, fibers are coated with carbon either by chemical vapor deposition or through pyrolysis of organic precursors prior to composite manufacturing. A post treatment at moderate temperatures volatilizes the carbon interphase by oxidation and leaves a narrow gap between matrix and fibers [4,33]. Since there is virtually no contact between matrix and fibers, this concept has the drawback of significantly reducing the load transfer between both components, which reduces composite strength [2]. Additionally, during long-term applications at high temperatures, embrittlement of the composite due to the strengthening of the interfaces may occur, since there is no barrier against chemical reaction and bonding between matrix and fibers [4].

Porous coatings (Figure 2(c)) are also a viable concept for crack deflection in CMCs, being most commonly used in all-oxide systems. They can be formed by coating the fibers with a mixture of oxide and carbon particles. After processing the composite, carbon is burned out, leading to an interphase with controlled porosity [34,38]. The bonding between fiber and matrix is strong at the contact