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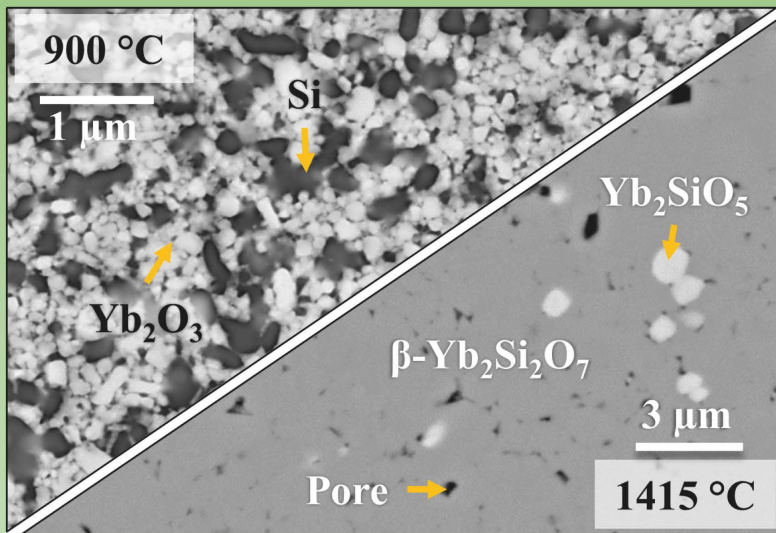
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***In situ* generated β -Yb₂Si₂O₇ environmental
barrier coatings to protect non-oxide
silicon-based ceramics in gas turbines**





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to protect non-oxide silicon-based ceramics in gas turbines





***In situ* generated β -Yb₂Si₂O₇ environmental barrier
coatings to protect non-oxide silicon-based ceramics
in gas turbines**

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1 Introduction and motivation

Over the last two centuries, economic growth has been driven at the expenses of the environment. In a scenario where the demand for energy constantly grows, fossil fuel-fired power generation still accounts for over 70% of the greenhouse gas emissions, caused mainly by the combustion of coal and oil. According to the International Energy Agency (iea), energy-related CO₂ emissions should be cut in half by 2050 compared to 2009 to limit the increase in the world average temperature by 2 °C. Despite the advances in renewable energy alternatives, their supply is strongly dependent on favorable weather conditions and their efficient storage is still difficult. Thus, the key factor for the transition towards a more sustainable future relies on decarbonizing power generation. Alone the substitution of heavy fossil fuels by natural gas is able to decrease the related emissions in approximately 50% [1–4]. Nevertheless, a developing interest has been shown for carbon-free fuel sources as ammonia and liquid hydrogen, which are potential alternatives to produce energy with a cleaner emission profile. However, the low heat of combustion and flammability of ammonia and the economically efficient storage and transport of liquid hydrogen still remain unsolved challenges for their sustainable utilization [5].

Besides the compactness, gas turbines can operate with versatile fuel sources and produce energy with high efficiency. For this reason, they have found increasing service in the past 60 years in the power industry both among utilities and industrial plants as well as for aviation throughout the world [6]. In combined cycle operation and with inlet temperatures exceeding 1400 °C, efficiencies as high as 63% can be achieved [2]. Therefore, different strategies are adopted to protect the currently used Ni-based superalloys such as the deposition of yttria-stabilized-zirconia thermal barrier coatings (TBC) and intensive film cooling. This standard is, however, not realistic when considering service for considerable amount of times ($t > 10,000$ h), since the great mismatch between the coefficient of thermal expansion (CTE) of the TBC and the alloy increase the risk of coating spallation and limit the application of metal-based components in turbine engines [7–10]. Especially envisioning the use of carbon-free fuel sources in future gas turbines, water vapor is one of the main products of combustion, which intensifies the degradation of these alloys [5,11–13]. Hence, advances towards reduced greenhouse gas emissions and more efficient gas turbines require their substitution by more robust materials resistant to oxidation and corrosion, able to endure service at higher temperatures.

Due to the reduced density, lower CTE ($3 - 5.5 \cdot 10^{-6} \text{ K}^{-1}$), high temperature creep resistance and melting points, non-oxide silicon-based ceramics as Si_3N_4 , SiC and SiC/SiC composites stand out for application in combustion environments [14–21]. In oxidative environments, the formation of a thermally grown SiO_2 -scale ensures a great oxidation stability. Nevertheless, $\text{H}_2\text{O}_{(\text{v})}$ reacts with this scale at temperatures above 1200°C , leading to corrosion and the rapid recession of the ceramic surface. Over the last three decades, progress has been made to develop reliable environmental barrier coatings (EBC) to hinder these detrimental effects [19,22–26]. Among the suitable EBC materials, rare-earth silicates have gained attention due to a high temperature endurance of at least 1400°C and very low SiO_2 activity [10,19,27–29]. Despite the higher corrosion rates of the disilicates in comparison with monosilicates, the lower CTE results in a better thermomechanical compatibility to Si_3N_4 , SiC and SiC/SiC substrates and should be considered when designing a reliable EBC for gas turbines. In special, yttrium disilicate ($\text{Yb}_2\text{Si}_2\text{O}_7$, $\text{CTE} = 3.91 \cdot 10^{-6} \text{ K}^{-1}$) exhibits no polymorphic transition and is therefore an attractive EBC candidate [19,27,30,31].

Despite the suitable protection against corrosion, the diffusion of oxygen through the EBC during long-term service at high temperatures leads to the oxidation of the substrate and jeopardizes the mechanical stability of coated systems [32,33]. Therefore, thermomechanical compatible bond-coats based on mullite ($\text{CTE} = 5.71 \cdot 10^{-6} \text{ K}^{-1}$) or silicon ($\text{CTE} = 4.1 \cdot 10^{-6} \text{ K}^{-1}$) are applied [10,19,27,34–36]. In comparison with mullite, silicon bond-coats are dense and can effectively hinder the diffusion of oxygen by forming a slow-growing SiO_2 -scale ($\text{CTE} = 3.1 \cdot 10^{-6} \text{ K}^{-1}$, β -cristobalite). Moreover, they have been reported to enhance adhesion, whereas oxide coatings usually exhibit an insufficient bonding strength to non-oxide silicon-based ceramics [10,27,37].

The most common techniques for the deposition of EBC systems onto non-oxide silicon-based ceramics are plasma spray [10,27,34,38], chemical (CVD) [39,40] or physical vapor deposition (PVD) [20,24]. PVD and CVD techniques are usually denoted by the very low deposition rates ($1 \mu\text{m h}^{-1}$), requiring extended processing times to achieve thick coatings [41]. The main disadvantages of plasma spraying lie within the evaporation of silica from the rare-earth silicate feedstock powder and in the rapid cooling rates during the coating deposition, resulting in an inhomogeneous phase composition and an amorphous microstructure. Due to the amorphous microstructure, plasma-sprayed coatings usually require a post-processing treatment at temperatures exceeding 1200°C and annealing times of over 24 h in air to enable phase crystallization [27,34]. Besides the energy and time-consuming procedures, another main drawback of the mentioned techniques is the difficult coating of complex geometries, as



required for gas turbines. In contrast, slurry-based techniques such as sol-gel or the polymer derived ceramics (PDC) enable the deposition of coatings by simple methods as spraying, spin- or dip-coating [42–46].

In special, the PDC route relies on the use of reactive silicon containing precursors as silazanes, carbosilanes and siloxanes. After or during the shaping process, a thermal treatment at low temperatures induces cross-linking, resulting in a thermoset, whereas further heating at above 400 °C yields a stable ceramic. Among the available precursors for coating application, silazanes stand out due to the commercial availability, high ceramic yield, strong adhesion to most substrates and high stability in oxidative and corrosive media [42,43,47]. Nevertheless, the protection of silazane-based coatings in such media often relies on the formation of a passivating SiO₂-scale, which undergoes detrimental reaction with water vapor in combustion environments. Moreover, mass loss and densification during the polymer to ceramic transition cause a volume shrinkage exceeding 50% [42,48], limiting the applicable thickness of crack and pore-free coatings to only a few micrometers [49,50]. The adverse effects related to the precursor shrinkage can be overcome by the use of fillers, hence enabling the deposition of thicker coatings with tailored properties [43,48,49,51–53].

These fillers are usually classified as passive, active and meltable. In contrast to passive fillers, active fillers undergo reaction with the atmosphere, precursor or pyrolysis products, thus expanding in volume and yielding tailored ceramic phases. The main role of meltable fillers is to act as densifying agents during melting, sealing porosity and relaxing stresses due to CTE mismatches at high temperatures. Consequently, the deposition of dense coatings of up to 100 µm for protection of steel substrates against oxidation and corrosion up to 700 °C was achieved [51]. Moreover in previous work [54], it was demonstrated that silazanes react with rare-earth oxides (RE₂O₃, RE = Y or Yb) as active fillers during pyrolysis in air to yield the respective silicates according to Eq. 1.1.1 and 1.1.2. Due to the shrinkage of the silazane precursor during pyrolysis, crack-free but porous coatings could only be obtained by limiting its amount, whereas the deficit of silicon resulted in unconverted rare-earth oxides.



A similar coating strategy was reported for the generation of ytterbium mono- and disilicate coatings on Si₃N₄ by the reaction of a polysiloxane and Yb₂O₃ during pyrolysis. The Si₃N₄ substrate was coated by dipping, followed by pyrolysis at 1000 °C in air and sintering at

1500 °C in N₂ atmosphere, achieving a coating thickness of 20 µm. However, no information about the formed crystalline phases was provided. Moreover, the coatings rapidly spalled-off during hot gas corrosion tests at 1450 °C for 200 h ($p = 1 \text{ atm}$, $p_{\text{H}_2\text{O}} = 0.18 \text{ atm}$ and $v = 100 \text{ m s}^{-1}$) due the residual porosity and insufficient adhesion to the substrate [55].

1.1 Goals

As mentioned before, ytterbium disilicate (Yb₂Si₂O₇) is a very attractive material for the protection of non-oxide silicon-based ceramics in combustion environments due to the matching CTE, very low corrosion rate and no polymorphic crystalline transition. Plasma spraying, PVD and CVD are typical techniques for the deposition of EBCs, denoted by the energy and time-consuming procedures. By contrast, the PDC route stands out due to the low-cost and uncomplicated application of coatings by typical lacquer techniques based on reactive silicon-containing precursors. Despite the excellent adhesion and the proven potential of silazane-based coatings for protection of ceramic and metal substrates against oxidation and corrosion in harsh environments, the formation of SiO₂ limits their application in combustion environments. In this context, the conversion of forming SiO₂ into hot gas corrosion resistant phases like rare-earth silicates is imperative to increase the stability of silazane-based coatings.

As will be presented in Section 2.8, the high reactivity of silazanes with ytterbium oxide (Yb₂O₃) leads to the efficient formation ytterbium silicates upon pyrolysis in air. Nevertheless, monolithic samples based on this system are characterized by a high porosity content ($\approx 40 \text{ vol\%}$) [54]. In addition, stable but porous coatings can only be achieved by limiting the fraction of silazane, which results in considerable amounts of unconverted ytterbium monosilicate (Yb₂SiO₃) and Yb₂O₃ after pyrolysis. Due to the high CTE mismatch of these phases with non-oxide silicon-based ceramics, associated with the porous coating microstructure, only a limited protection against hot gas corrosion can be expected in combustion environments. Based on these premises and regarding the customary techniques for EBC application, the main goal of this work consisted in developing a straightforward and easier approach for the deposition of Yb₂Si₂O₇ coatings by the PDC route to hinder hot gas corrosion of non-oxide silicon-based ceramic components.

During the pyrolysis step of silazane-based coatings, their microstructure, composition and mechanical properties can be strongly influenced by the substrate. Therefore, the development of a slurry and the assessment of suitable pyrolysis parameters to yield dense and crystalline Yb₂Si₂O₇ should occur without the influence of a substrate by processing free-



standing samples as powder and monoliths. Subsequently, coating experiments should be carried out with a non-oxide silicon-based ceramic substrate (i.e. Si_3N_4 , SiC or SiC/SiC). In order to enable a straightforward and easy coating application, the largest coating thickness should be obtained with the lowest number of steps to reduce the processing time. In addition, the influence of the selected substrate on the resulting coating properties should be investigated.

During service in gas turbines, water vapor is a main product of combustion, which composes approximately 10% of the atmosphere. Corrosion by water vapor at above 1200 °C and a flow velocity that can exceed 100 m s⁻¹ lead to the rapid volatilization of SiO_2 and the considerably high recession rates of ceramic components [11,15]. Besides hot gas corrosion, changes in the operating conditions of gas turbines such as starting or an emergency shut-down can cause harsh thermal shocks of more than 800 K within one second, leading to the evolution of additional thermal stresses [56], which must be endured by the coating system during the life expectancy of the components in gas turbines ($t > 10,000$ h). During the evaluation of the performance of the coating system in turbine-like environments, it should remain well-adhered and reduce hot gas corrosion regarding uncoated substrates.

Since gas turbines are expected to operate for considerable amount of times and rare-earth silicate-based environmental barrier coatings are slowly corroded in hot gas environments, the deposition of thick coatings ($> 100 \mu\text{m}$) is desired to extend the life span of coated ceramic parts. To obtain a coating system with high thickness, strong adhesion, low residual porosity and high thermomechanical stability are the greatest challenges of PDC processing, since most PDC-based coatings are limited to a few microns in thickness. Thus, alternatives should be sought to increase the achievable thickness of the PDC-based $\text{Yb}_2\text{Si}_2\text{O}_7$ coating. At last, coating experiments should be carried out with other non-oxide silicon-based ceramics, followed by the characterization of the resulting microstructure and composition to evaluate the transferability of the developed coating technology.