INTRODUCTION

Alumina is a ceramic oxide with excellent properties, such as high strength, hardness, corrosion, chemical stability, and wear resistance.\textsuperscript{1–3} High purity alumina bodies usually require high sintering temperatures—usually over 1400°C—to reach relative densities close to 100%.\textsuperscript{4} Additives—such as TiO\textsubscript{2}, MnO, MgO, Cu\textsubscript{2}O, ZrO\textsubscript{2}, Y\textsubscript{2}O\textsubscript{3}, and Li\textsubscript{2}O\textsubscript{3}—have been employed to increase alumina sinterability and achieve full density while controlling grain growth.\textsuperscript{5,6} Sintering aids can enhance sintering due to the formation of lattice defects, solid solutions, or liquid phases. Generally, there is an optimal amount of additives, which varies with the sintering temperature to achieve higher densification.\textsuperscript{7,8}

TiO\textsubscript{2} is a crystal growth promoter and sintering aid for alumina. Even small amounts (0.2 mol\%) can effectively enhance diffusion,\textsuperscript{9} particularly at grain boundaries. For submicrometric titania, a gradual change was observed

Dopant diffusion at the interface of TiO\textsubscript{2}-MnO-doped alumina/alumina layers in sintered laminates

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Abstract

Ceramic laminates were produced by thermal pressing of pure alumina (Al\textsubscript{2}O\textsubscript{3}) and TiO\textsubscript{2}-MnO-doped alumina (d-Al\textsubscript{2}O\textsubscript{3}) tapes and subsequently sintered at temperatures ranging from 1100 to 1250°C. The diffusion of dopants through the interface was investigated by optical (OM), scanning electron (SEM) microscopy, nanoindentation, and energy-dispersive X-ray spectroscopy (EDS) together with scanning transmission electron microscopy. Temperature-dependent dopant diffusion and porosity profiles were, respectively, observed investigating the microstructure. For d-Al\textsubscript{2}O\textsubscript{3}, the average grain size, hardness, and Young's modulus were higher when compared to pure alumina, while the dopants diffusion zone presented intermediate values of these properties. The increase in sintering temperature resulted in higher values of hardness and Young's modulus in both layers. A further investigation showed a gradual decrease in grain size, hardness, and Young's modulus from the doped to the pure alumina layer, corresponding to a decreasing gradient in the dopants concentration in the Al\textsubscript{2}O\textsubscript{3} layer with increasing distance from the interface. High concentrations of Mn and Ti were observed at triple points and grain boundaries, as well as within alumina grains.

KEYWORDS
alumina, diffusion, dopants, interface, manganese oxide, nanoindentation, titanium dioxide

1 INTRODUCTION

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TiO\textsubscript{2} is a crystal growth promoter and sintering aid for alumina. Even small amounts (0.2 mol\%) can effectively enhance diffusion,\textsuperscript{9} particularly at grain boundaries. For submicrometric titania, a gradual change was observed
from grain-boundary to volume diffusion with increased titania content.\textsuperscript{10} For particle sizes between 1 and 2 µm, sintering occurred by a combination of both mechanisms. For coarser alumina (>2 µm), the sintering mechanism observed was grain-boundary controlled regardless of titania content.

MnO has been used as a sintering aid to alumina in amounts as low as 0.3% by promoting volume diffusion. When even lower MnO amounts are used, a tendency of grain-boundary diffusion was observed.\textsuperscript{11} Toy et al\textsuperscript{12} verified for alumina doped with MnO no secondary phase formation and deduced that a solid solution with Al\textsubscript{2}O\textsubscript{3} is formed. Cutler et al\textsuperscript{13} showed that MnO together with TiO\textsubscript{2} is more effective in lowering the alumina sintering temperature than using these additives alone. They also reported evidence of a liquid phase formation that accelerates densification. Alternatively, Jones and co-authors\textsuperscript{14} suggested that anion and cation vacancies in the alumina lattice would increase the rate of diffusion and sintering.

A previous work\textsuperscript{15} on doped-undoped alumina laminates sintered at 1200\textdegree C briefly reported the diffusion of dopants along with the interface. However, in that case, the main focus was the laminate design and the respective mechanical behavior. In another work, the stability and rheology of colloidal suspensions of undoped and doped alumina suspensions were studied.\textsuperscript{16} In the present work,
the diffusion of TiO₂ and MnO as densification aids at the interface of doped and undoped Al₂O₃ layers sintered as laminates at different temperatures is investigated in detail.

2 | MATERIAL AND METHODS

High purity alumina (99.99 wt% Al₂O₃, Taimicron TM-DAR, d₅₀ = 150 nm, Taimei) and a mixed powder with a final average particle size of 220 nm of the same alumina doped with 1.68 wt% titanium dioxide (TiO₂, Kemira) and 2.32 wt% manganese oxide (MnO, Sigma-Aldrich) were added to deionized water to produce 21 vol% solids slurries in a ball mill. Additionally, 30 wt% of binder (Mowilith LDM 6138, Celanese), 2 wt% of dispersant (Darvan C-N, Vanderbilt Minerals), 1.5 wt% of nonionic surfactant (Ninol PK-80 BR, Stepan), and 1 wt% of antifoamer (Antifoam Y-30, Sigma-Aldrich) were added referred to solid content. Slurries were cast in a table-top tape caster (CC-1200, Tape Casting Warehouse) and left to dry for 24 hours at room temperature.

Ceramic laminates composed of outer pure alumina layers (Al₂O₃) and an intermediate layer of doped alumina (d-Al₂O₃) were produced by uniaxial pressing at 10 kN and 65°C for 5 minutes. Samples were first debinded at 600°C for 1 hour with a heating rate of 0.3°C/min. They were later sintered
in air at 1100, 1150, 1200, and 1250°C for 2 hours, with heating and cooling rates of 5 and 10°C/min, respectively. Samples were embedded with an acrylic resin (Scandiquick, Scan-Dia), ground with silicon carbide papers, and polished with diamond suspensions (Struers) with the last grains size of 0.25 µm. After nanoindentation tests, the samples were removed from the resin and submitted to thermal etching at 90% of the sintering temperature for 30 minutes to reveal the grains. The microstructure was analyzed by optical (OM, BX51, Olympus) and scanning electron (SEM, Supra VP 55, Zeiss) microscopy. The line-intercept method was applied to measure grain size (at least 200 grains per sample) using software for image analysis (Lince 2.4.2e, Ceramics Group, TU Darmstadt).

Hardness (H) and Young’s modulus (E) were measured using a nanoindenter equipped with a Berkovich tip (G200, Agilent Technologies) for pure and doped layers, and the diffusion region between them. Nanoidentation was performed on polished-surface samples by continuous stiffness measurement (CSM) with a constant strain target of 0.05 s⁻¹, a harmonic displacement target of 2 nm, and a harmonic frequency of 45 Hz. The maximum depth was set to 2000 nm, with a holding time of 10 seconds before unloading. At least 10 measurements were carried out for each region in each sample.

To investigate E and H profiles along the region of dopant diffusion, six batches of 19 indentations were performed in the 1200°C-sintered sample along with the interface from the d-Al₂O₃ layer to the Al₂O₃ layer. Tests were done with an advance of 7.5 µm and lateral displacement of 60 µm related to the last indentation. Additionally, the grain size profile was also measured in the same region using the line-intercept method. Measurements were done with an advance of 5 µm from the last point, in a total of 18 points. For each point, a straight line was drawn parallel to the interface and at least 30 grains per line were measured. The procedure was repeated two times.

X-ray diffraction was performed at room temperature in a diffractometer (Miniflex, Rigaku Corporation) in the 2θ angle range varying from 5° to 90°, and crystalline phases were characterized using a database (PDF-2, ICDD). The energy-dispersive X-ray spectroscopy (EDS, AZtecLive, Oxford Instruments) was performed with the help of a scanning transmission electron microscope (STEM, Helios NanoLab G3, FEI™) to investigate dopants diffusion in doped alumina.

### RESULTS AND DISCUSSION

Figure 1 presents OM and SEM images for sintered samples exhibiting a light brownish region in the Al₂O₃ layer close to the d-Al₂O₃ layer. The higher the sintering temperature, the more accentuated is this effect and thicker is the region. This color change is the first hint for the diffusion

| Sintering temperature (°C) | Pure alumina | Interface | Doped alumina |
|---------------------------|--------------|-----------|---------------|
| 1100                      | 120 ± 7      | 202 ± 6   | 253 ± 10      |
| 1150                      | 214 ± 15     | 361 ± 53  | 542 ± 33      |
| 1200                      | 335 ± 28     | 639 ± 34  | 835 ± 21      |
| 1250                      | 521 ± 29     | 576 ± 31  | 848 ± 1       |
of the dopants. Thereby, the degree of diffusion of dopants depends on the temperature of sintering. Dopants have a threshold distance from the interface to diffuse, resulting in a diffusion region with regular thickness. The optically estimated thickness for each sample was 17 ± 2 µm for 1100°C, 25 ± 3 µm for 1150°C, 51 ± 7 µm for 1200°C, and 62 ± 10 µm for 1250°C.

Figure 2 presents the average grain size for each layer at the different sintering temperatures. The SEM images show that the diffusion of dopants modifies the microstructure of the pure alumina layer, for example, larger grains in the diffusion zone. Doped alumina presented larger grains with increasing sintering temperature. Significant grain coarsening is observed at 1250°C for the doped alumina layer. On the other hand, pure alumina presents smaller grains when compared to doped alumina, with no significant variation of the average grain size at the respective sintering temperatures.

It is useful at this point to mention what is known about bulk and grain-boundary diffusion in alumina. As noted in a review by Heuer,17 bulk diffusivity data exhibit a clear trend in an Arrhenius representation for oxygen and aluminum diffusion in Al₂O₃ in the temperature range of 1200 to 1800°C. Obviously, the higher the temperature, the higher the bulk diffusion, still remarkable diffusion data were observed in the range of 1200-1400°C.18,19

Figure 3 shows the typical load-displacement nanoindentation curves obtained for each sample in the three tested regions. Table 1 complements the figure and presents the average maximum loads achieved during tests. It is observed that the higher maximum loads for each sintering temperature are attributed to d-Al₂O₃ layers, while the lower ones are for Al₂O₃ only. Interfaces show always a maximum load between values of pure and doped alumina. In most cases, the load reached the preset maximum value, 2000 mN. Therefore, a plateau is observed after curves reach the maximum load, indicating that displacement still occurs during the holding period, which is most likely caused by creeping deformation.20 In general, maximum loads are supposed to increase with increasing sintering temperatures, which is related to the densification of layers. Still, the maximum load value at 1200 and 1250°C, respectively, for doped alumina layers exhibits little gain.

| Sintering temperature (°C) | Young's modulus (GPa) | Hardness (GPa) |
|---------------------------|-----------------------|----------------|
|                           | Pure alumina | Interface | Doped alumina |
|                           | Pure alumina | Interface | Doped alumina |
| 1100                      | 57 ± 3       | 83 ± 2    | 99 ± 4        |
| 1150                      | 83 ± 4       | 130 ± 1   | 171 ± 9       |
| 1200                      | 116 ± 7      | 195 ± 11  | 235 ± 12      |
| 1250                      | 159 ± 7      | 193 ± 8   | 283 ± 14      |

**Table 2** Young's modulus and hardness for pure alumina, interface, and doped alumina regions, according to the sintering temperature

**Figure 5** Young's modulus and hardness profile in the sample sintered at 1200°C. The gray line and light gray zone represent, respectively, the average values and standard deviation for d-Al₂O₃ reference. The pink line and light pink zone represent, respectively, the average values and standard deviation for Al₂O₃ reference. The X-axis indicates the distance from the first point (point zero), which starts in the doped alumina layer and advances in the direction of the pure alumina layer.
Figure 4 and Table 2 present the average Young's modulus (E) and hardness (H) obtained for each region at the different sintering temperatures. Again, an increase of these properties is observed with increasing sintering temperatures, which is related to the higher degree of densification of samples. The interface of the sample sintered at 1200 and 1250°C presented no significant changes in E and H.

Figure 5 presents the nanoindentation results along the diffusion profile carried out for the sample sintered at 1200°C. Along the region of diffusion, a gradual transition of Young's modulus and hardness values is observed. In the pure layer close to the interface, the concentration of diffused dopants in the alumina layer is highest and decreases further away from the interface resulting in respective gradients of the sintering potential. As well known, the porosity gradient caused thereby has a deleterious influence on Young's modulus and hardness. Previous work already presented the values of relative density for doped and alumina sintered at 1200°C, 98% and 79%, respectively.15 As the distance from the interface increases, the amount of dopants decreases until no diffusion occurs. Higher sintering temperatures provide more energy to the system. The higher the temperature, the further the distance the dopants travel, and consequently, the higher the thickness of the diffusion region. This also explains the intermediate values of E and H obtained for the interface in all sintering temperatures, compared to the Al₂O₃ and d-Al₂O₃ layers.

Moreover, there is also a gradual decrease in grain size from the interface toward the pure alumina (Figure 6). Since the dopants act as a sintering aid and crystal growth promoter, the higher amounts of dopants result in larger grain sizes, as observed in Figure 7.

Figure 8 shows the X-ray diffraction spectra of doped and undoped alumina layers sintered at 1200°C. In both layers, alumina is presented in the rhombohedral crystal-line structure, α-alumina. In the doped alumina sample, there is evidence of the presence of titanium dioxide (rutile) and the formation of manganese titanate. MnTiO₃ is reported to occur in the MnO-TiO₂ phase diagram for the mole ratio from 0.33 to 0.5 up to ~1385°C.21 For d-Al₂O₃,
The presence of MnTiO3 is in agreement with the EDS-STEM mapping analysis (Figure 9). The micrograph shows the presence of closed intergranular pores (black points) located in the triple points of alumina grains (dark gray). The dopants (light gray) settled mainly in the triple points and grain boundaries of alumina grains, indicating that the dopant level exceeds essentially the amount of dopants, which form a grain-boundary film. Additionally, dopants are also located as intragranular inclusions within alumina grains. EDS mapping evidenced the high concentration of Mn and Ti in these regions (light gray points). This behavior indicates that these segregations did not pin the grain boundaries during grain coarsening.

**FIGURE 9** STEM micrograph of doped alumina layer sintered at 1200°C. Alumina grain appears in dark gray, pores in white, and dopants in light gray. Below is presented an EDS mapping analysis of the blue square region of the micrograph. The colors blue, red, yellow, and purple refer to the presence of aluminum, oxygen, manganese, and titanium, respectively. EDS, energy-dispersive X-ray spectroscopy; STEM, scanning transmission electron microscope

**4 | CONCLUSIONS**

In this work, the diffusion of dopants in TiO_2-MnO-doped Al_2O_3/Al_2O_3 laminates was investigated using scanning
electron microscopy, optical microscopy, EDS, and nanoindentation. Optical micrographs showed the presence of a light brownish region in pure alumina layers due to the presence of dopants that migrate from doped alumina layers. The diffusion region could be optically estimated and increased with increasing temperatures. The SEM images showed modifications on the microstructure of pure alumina due to the presence of dopants. The average grain size of d-Al₂O₃ is higher than those of Al₂O₃ at all sintering temperatures. Higher values of maximum load, hardness, and Young’s modulus were observed for d-Al₂O₃ layers, compared to Al₂O₃ layers. The dopants diffused zone presented intermediate values to that observed for doped and pure alumina layers, due to modifications in the microstructure caused by Ti and Mn.

According to the accurate analysis of the diffusion zone done for the sample sintered at 1200°C, the concentration of dopants is high right after the interface and decreases gradually for longer distances until no significant dopant effects are detectable. XRD analyses detected α-alumina in both layers, as well as titania as rutile, and evidence of MnTiO₃ formation in d-Al₂O₃. Also, EDS/STEM showed the presence of intergranular closed pores and dopants settled in intergranular and intragranular positions, corroborating with the fact of Ti and Mn diffused through the alumina.

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