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ATZ Composites Resistant to Subcritical Crack Propagation

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Abstract

ATZ (alumina toughened zirconia) particulate composites are materials which utilize the phenomenon of residual thermal stresses arising during cooling from the sintering temperature to normal conditions. Since the stresses in zirconium dioxide grains are tensile, they increase the susceptibility to transformation of the tetragonal phase into the monoclinic one, a phenomenon which is used to strengthen the material, i.e. to increase its resistance to cracking. The paper presents the results of research on composites that were manufactured by means of special technology using the sintering of a mixture of ZrO_2 powders with various contents of the stabilizing oxide Y_2O_3. These materials, thanks to a significant reduction in grain size, demonstrate excellent mechanical parameters, strength and resistance to brittle fracture. Moreover, it was found that incorporating alumina grains in the zirconia matrix can cause the distribution of stress to significantly reduce the tendency to subcritical cracking, which is a high risk for oxide ceramics. It was found that for some ATZ composites the phenomenon of subcritical cracking was inhibited in both air and water environments.

Keywords: particulate composites, zirconia, alumina, fracture toughness, subcritical crack propagation

Introduction

Zirconia (ZrO_2) and alumina (Al_2O_3) are two of the most widely used ceramic materials in various engineering applications owing to their excellent mechanical properties, such as high strength, hardness, and wear resistance [1-3]. However, these materials also have some disadvantages, for instance, low fracture toughness and poor thermal shock resistance, which limit their use in certain applications. To overcome the limitations of each of the above-mentioned materials and offer improved mechanical properties, researchers have extensively studied and developed zirconia-alumina composites over the past few decades [4-10]. This has led to significant advancements and commercialization of these

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composites in various industries. Beyond their traditional applications as machinery parts in engineering, zirconia-alumina composites have also found important biomedical applications, such as hip joints and dental restorations [10-16].

Commercially, these materials most often use the tetragonal phase of zirconium dioxide, which benefits from a unique physical phenomenon: the ability to toughen through martensitic transformation of the tetragonal phase into a monoclinic one [17, 18]. This transformation is a very effective method for strengthening polycrystalline ceramics. When manufacturing composites containing the tetragonal phase of zirconium dioxide, this phenomenon can be combined with other factors to enhance crack resistance. These additional factors include residual stresses related to the mismatch of the thermal expansion coefficients of the component phases [19-21] and the interaction of a crack propagating in the matrix with the dispersed phase inclusions [22].

One of the critical issues in oxide materials operating under long-term loads is the undesirable slow crack propagation, which leads over time to decreased strength and increased susceptibility to brittle fracture [22-25]. Stress corrosion cracking, influenced by the presence of water molecules in the working environment, further exacerbates this problem. Subcritical cracking significantly limits the lifespan and applicability of these materials, which is not observed in non-oxide polycrystals such as carbides and nitrides [26]. Significant advancements in the technology of sintered oxide materials have led to the development of composites where subcritical cracking is either eliminated or remarkably reduced. These advanced materials incorporate zirconium dioxide and exploit the martensitic transformation phenomenon to enhance performance.

This study presents the preparation of an alumina-toughened zirconia (ATZ) composite in which subcritical cracking is inhibited by means of a specific sintering method. This method involves the use of two zirconia powders with differing yttrium stabilizing ion contents, which significantly modifies the composite microstructure and phase composition, leading to improved mechanical properties and durability.

Previous studies [27] demonstrated that the adopted method of producing ATZ composites enabled the creation of materials in which the phenomenon of subcritical cracking was significantly reduced (ATZ-B) or even eliminated (ATZ-10, ATZ-20). For the ATZ-B composite, prior water immersion tests were conducted, revealing a decrease in strength values for specific increments in stress compared to those tested in air. Nevertheless, the tendency for subcritical cracking, as indicated by the value of parameter *n*, remained consistent, suggesting that in both environments cracking belonged to the same range of crack velocity dependence on stress intensity factor K_I [28-30]. In the present study, the testing of composites with higher Al_2O_3 contents was supplemented with water immersion tests to verify whether this environment might induce subcritical cracking.

Materials and methods

The matrix of the base composite, referred to throughout the paper as ATZ-B, was synthesized using two different zirconia powders, both obtained via the "wet" preparation method. One powder consisted of pure zirconia, while the other was a solid solution containing 4 mol% yttria (Y_2O_3) in a crystalline structure.

To prepare these powders, a 1.2 M solution of pure zirconyl chloride, or a similar solution with added yttrium chloride to achieve a 4 mol% Y_2O_3 concentration in the solid solution, was incrementally introduced into a vigorously stirred ammonia solution (1:1 ratio). The resulting gels were thoroughly washed with distilled water to eliminate reaction by-products, followed by calcination at 600°C for one hour. Subsequently, the calcined gels were milled in a propyl alcohol medium using a rotary vibratory mill for two hours.

For the preparation of the base composite (ATZ-B), the two zirconia powders were blended in a proportion that resulted in a final yttrium oxide content of 3 mol%. Additionally, 1.5 wt% nanometric alumina (TM-DAR, Taimicron) was incorporated into the mixture. The blending process was conducted in a rotary-vibratory mill with propanol as the medium for 30 minutes. The initial powders had a particle size of 0.20±0.05 μm for Al_2O_3 and 0.04±0.01 μm for the synthesized ZrO_2.

The composite materials were prepared using a similar methodology with varying additions of alumina powder (TM-DAR, Taimicron) to the ATZ-B base. Specifically, the two composite materials, ATZ-10 and ATZ-20, were formulated to contain final corundum contents of 8.4 wt% and 15.8 wt%, respectively (Table 2). Each powder mixture sample underwent initial uniaxial pressing followed by isostatic pressing at 200 MPa. The sintering process was carried out in air atmosphere within a zirconia powder bed at 1450°C for two hours, utilizing a Nabertherm electric furnace.

The Rietveld procedure was employed to determine the quantitative contents of individual phases. The peaks corresponding to tetragonal zirconia, monoclinic zirconia and alumina were identified using JCPDS files. On the basis of known contents, the theoretical values of the densities were determined using the rule of mixtures. The apparent density was determined by means of the Archimedes method.

The microstructure observations were conducted using the scanning electron microscope Apreo 2S (Thermo Scientific, Netherlands). The Vickers hardness, HV, was determined utilizing a ZwickRoell hardness tester with a load of 9.81 N applied for 10 s. The Palmquist type crack lengths and the indent dimensions obtained in the hardness test under the 49.05 N load were used to determine the critical stress intensity factor, K_{Ic}. The calculations were based on the model developed by Niihara [31].

The strength measurements were conducted by means of a biaxial loading device according to the ASTM standard [32]. The tests were carried out at four stress rates 0.1, 1, 10 and 200 MPa/s, thirty samples each [33]. The obtained results are presented on double logarithmic flexural strength (σ) vs. stress rate ($\dot{\sigma}$) dependence graphs (Figure 2). If an increase in strength was observed with a rising stress rate, it could be attributed to the occurrence of subcritical cracking. Parameter *n*, which indicates the material's susceptibility to subcritical cracking, was determined based on the slope of the fitted line. The tests were conducted both in air and in water (at 20°C).

Results

Figure 1a-c presents the composite microstructures, where the bright grains are the zirconia matrix and the dark grains are the alumina inclusions. These materials have a small grain size of about 0.3 µm. It can be seen that the alumina is well distributed in the zirconia matrix and its growing amount is noticeable in the presented micrographs. Table 1 lists the density and mechanical properties of the investigated materials. The presented values show that the preparation procedure, including forming and sintering, resulted in high densification of the materials. The Vickers hardness values remained at the same level, despite the alumina content. The fracture toughness results indicate high resistance to cracking in comparison to typical tetragonal zirconia materials prepared from commercial powders [27].

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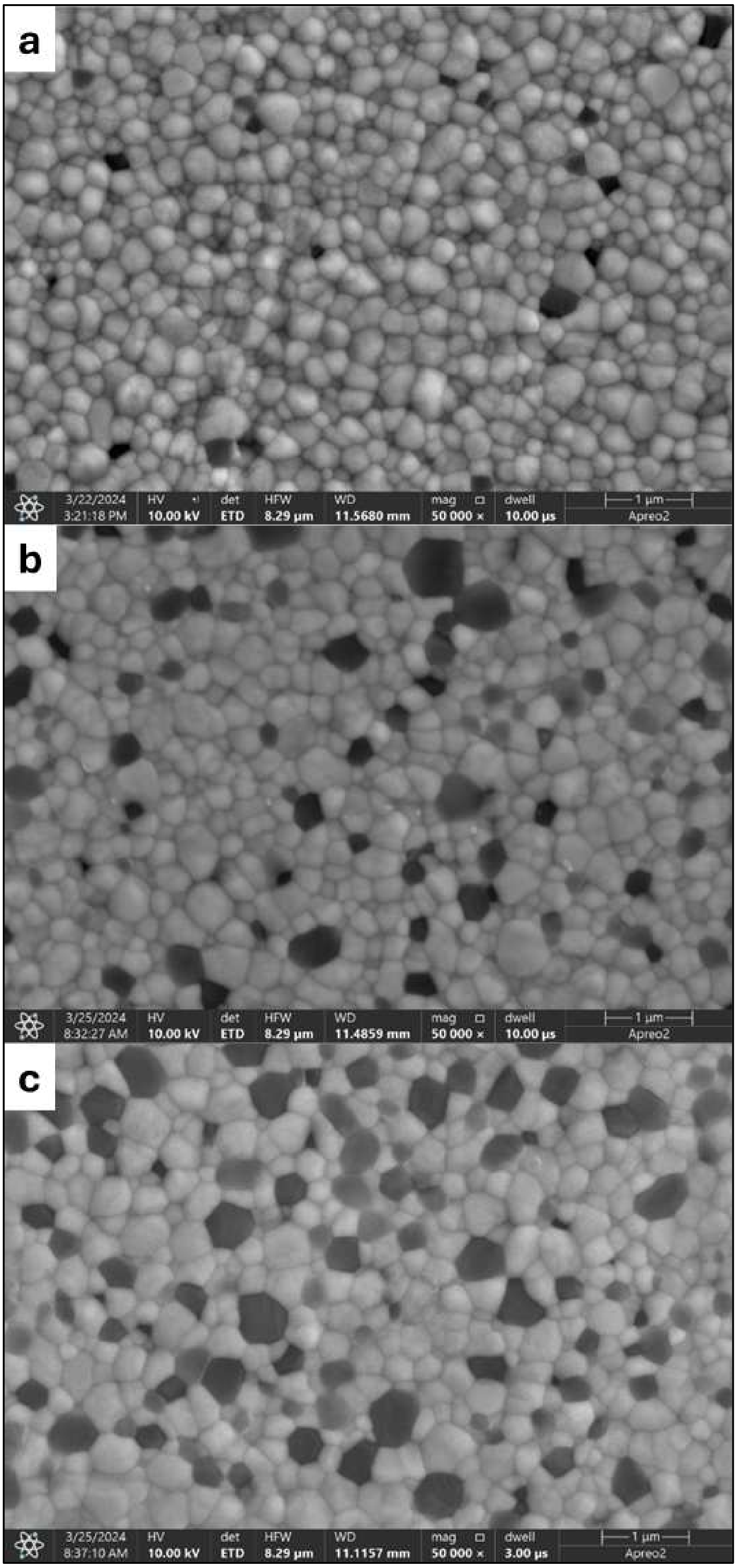

Fig. 1. SEM micrographs of: a) ATZ-B, b) ATZ-10 and c) ATZ-20 composites.

Table 1. Basic physical and mechanical properties of investigated materials [27].

Material	Apparent density [g/cm^3]	Theoretical density [g/cm^3]	Relative density [%]	Hardness HV [GPa]	Fracture toughness [MPa·m$^{1/2}$]
ATZ-B	5.99	6.01	99.63	12.0 ± 2.6	12.7 ± 0.8
ATZ-10	5.68	5.81	98.20	13.1 ± 2.6	9.8 ± 1.4
ATZ-20	5.58	5.61	99.46	13.8 ± 3.9	10.9 ± 2.6

Table 2. Phase compositions of investigated materials.
***t* – tetragonal zirconia, *m* – monoclinic zirconia, *a* - alumina**

	Phase composition in wt%		
	t	*m*	*a*
ATZ-B	88.3	10.8	0.9
ATZ-10	83.4	8.4	8.2
ATZ-20	78.6	5.7	15.7

Figure 2 presents the double logarithmic dependency between flexural strength, obtained in biaxial loading, and four different stress rates. In the ATZ-B composite, a slight increase in strength is observed with a longer testing time. This trend is consistent in both air and water environments – the n parameters are almost identical. What changes, however, is the strength, with the values obtained in water being lower than those in air. The examined ATZ-10 and ATZ-20 composites did not show any changes in strength during testing in air. Additionally, measurements were performed in water, which, despite the higher concentration of the corrosive agent at the crack tip, still did not show the occurrence of the phenomenon.

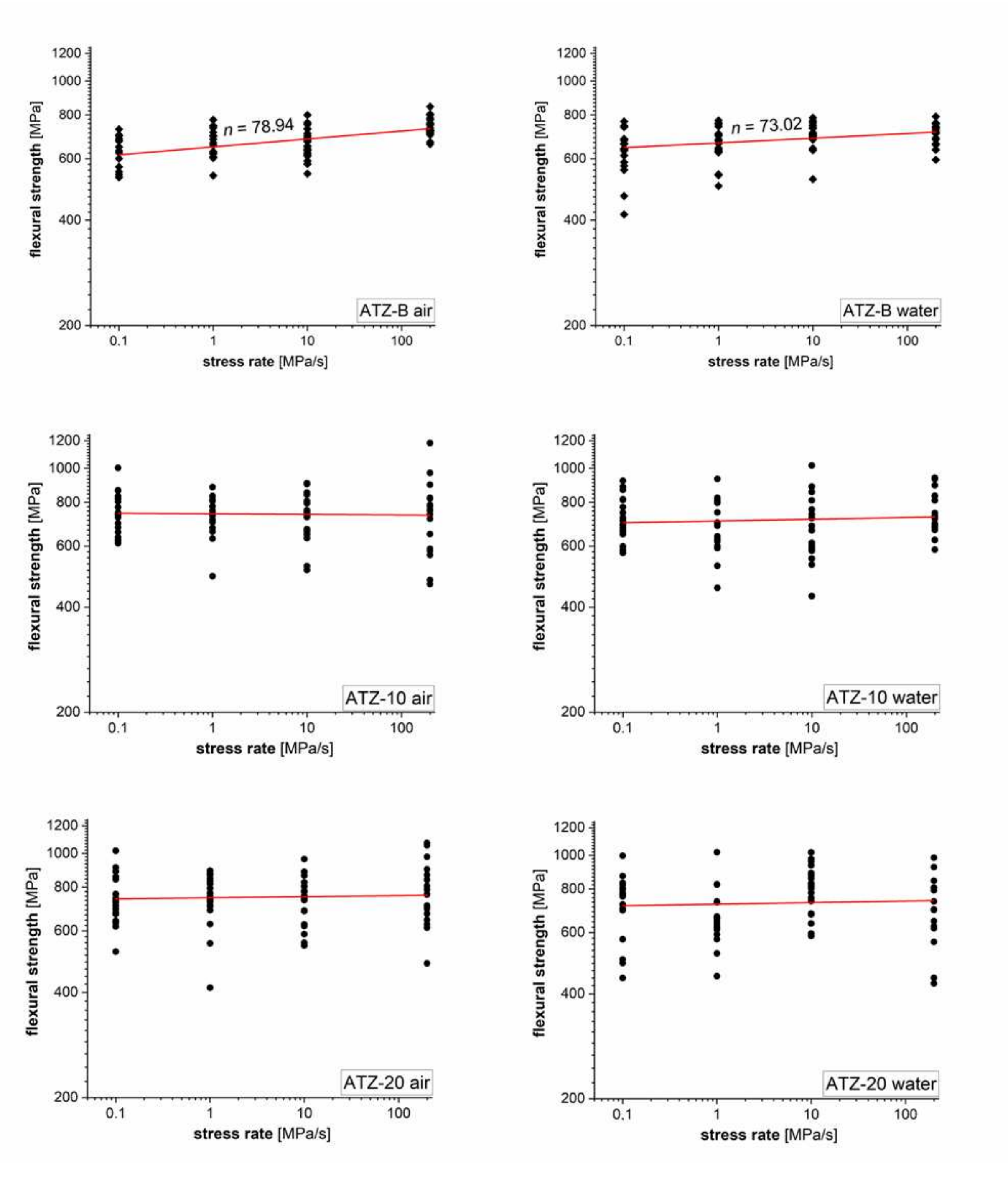

Fig. 2. Double logarithmic tendency between flexural strength and stress rate for ATZ-B [27], ATZ-10 and ATZ-20 composites tested in air and water.

In ZrO_2/Al_2O_3 composites due to the relationship between the thermal expansion coefficients of both phases, alumina is always under compressive stress, while zirconia is under tensile stress. Using Taya's formula to calculate the average stress values, we estimated these stresses for all the materials (Table 3) studied in this work [34]. It is evident that these values mainly depend on the phase content: the more

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corundum present, the lower the average stress in this phase. Similarly, the more zirconia present in the composite, the lower the average tensile stress in it. Macroscopically, this should result in the tendency for the tetragonal ZrO_2 phase transformation to increase with rising average tensile stress, i.e. with an increase in Al_2O_3 content. Nonetheless, we observe the opposite phenomenon. The greatest tendency for transformation is observed in the material with the negligible corundum phase content, and as this content grows, the transformation tendency decreases. This suggests that the average stress value is not the decisive factor in this case, but rather the difference between the average stress values. Previous studies [35] analyzing stress distribution showed that maximum stress gradients occur in the interphase boundaries between ZrO_2/Al_2O_3. These maximum gradients decline as the phase content becomes more balanced (with a rise in corundum content). Simultaneously, the proportion of interphase boundaries in the total number of grain boundaries naturally increases. It is most likely the combined effect of these factors that causes the increment in Al_2O_3 content in the composite to stabilize the phenomenon of subcritical cracking. This stabilization effect is also maintained in a water environment, which offers these materials interesting application prospects, both as structural ceramics for machine components and in biomedical applications.

Table 3. Average stress values for both phases in investigated materials.

Material	Compressive stress in corundum [MPa]	Tensile stress in zirconia [MPa]
ATZ-B	744	21
ATZ-10	545	90
ATZ-20	490	135

Figure 3 presents the cracks in the microstructures of the investigated materials introduced by the Vickers indenter. The micrographs present the crack tip and its surroundings. The first observation worth noticing is that the crack tip is thinner in the ATZ-10 and ATZ-20 than in the ATZ-B material. This might be an effect of clenching the crack due to the volume increase during the tetragonal to monoclinic phase transformation, which is more favorable in the composites with the higher alumina content [27]. What is more, in the ATZ-B material, microcracks located out of the main crack plane are relatively frequent (see Fig. 3a). This phenomenon was not detected in the ATZ-10 and ATZ-20 composites. It suggests that the cracking process was more “spontaneous” in ATZ-B than in the materials with the higher alumina content. In the last mentioned materials, the cracks propagated through the polycrystals were more uniformly distributed.

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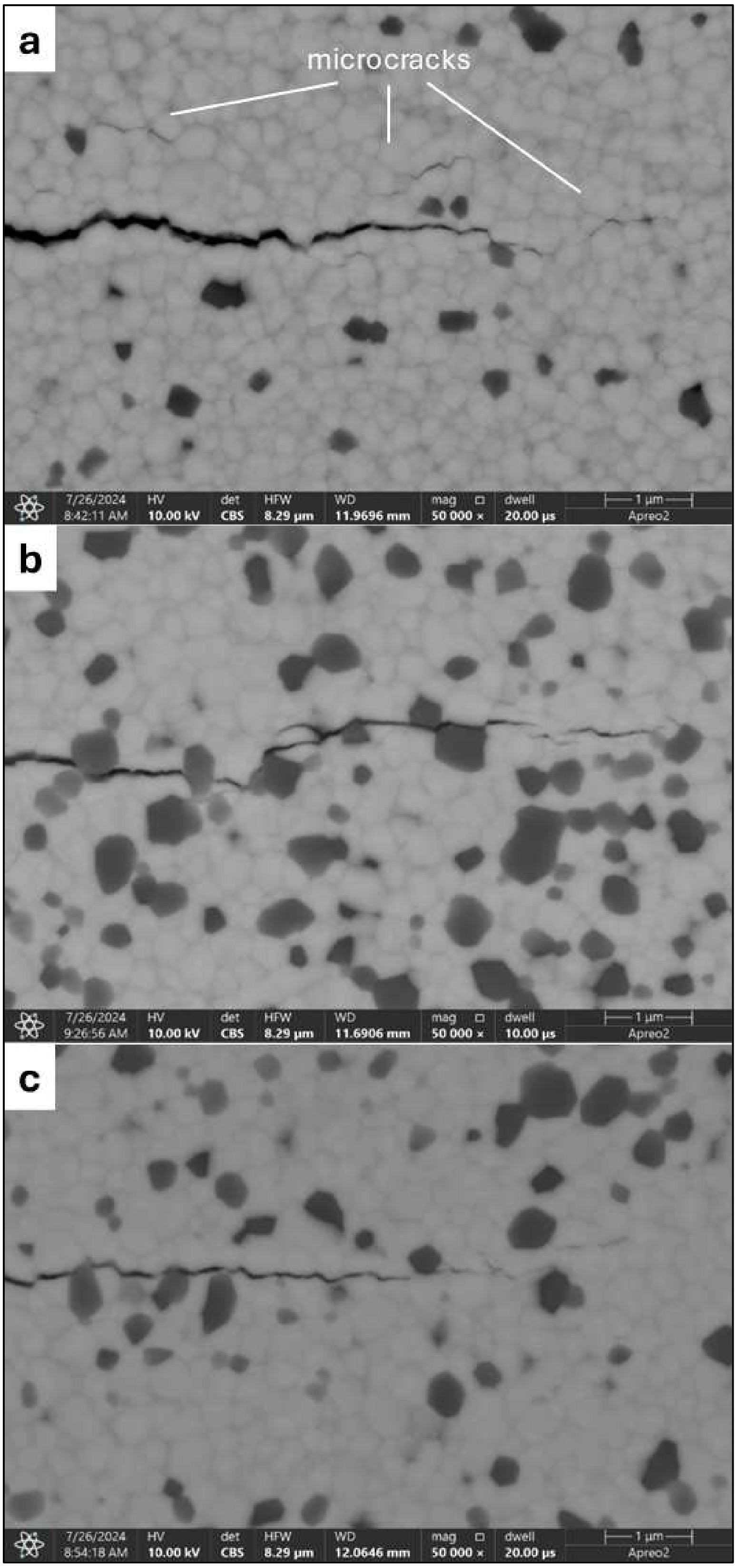

Fig. 3. SEM micrographs of: a) ATZ-B, b) ATZ-10 and c) ATZ-20 composites, with cracks introduced by Vickers indenter.

Conclusions

The subcritical crack growth tests demonstrated that both the ATZ-10 and ATZ-20 composites exhibit high resistance to this phenomenon. The microstructure of the composites, enhanced by the presence of alumina, impedes the slow propagation of cracks under subcritical conditions. This finding indicates that these materials are well-suited for applications requiring long-term reliability under sustained loads.

The high resistance to subcritical crack growth, inducing stable strength over time, suggests that the ATZ-10 and ATZ-20 composites have an extended operational lifetime compared to most oxide ceramic materials that are more susceptible to subcritical crack growth, not only in air, but also in a more aggressive environment – water.

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