Tougher and harder zirconia toughened alumina composites through *in situ* microstructural formation of LaMgAl11O19

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**ABSTRACT**

Advanced ceramic materials are highly demanded for various modern industrial and practical engineering applications. Nonetheless, the requirement of attainment hard and simultaneously tough materials is a crucial matter for industrial sectors. To accomplish this target, the strategy of designing a novel microstructure of Zirconia Toughened Alumina (ZTA) ceramics was utilised through *in situ* formation of LaMgAl11O19 (LMA) based on the stoichiometry ratio of constitute oxides inside ZTA composites during sintering process. ZTA Samples were conventionally sintered at 1600 °C for 2 hrs to ensure fully formation of LMA while their characteristics were analysed using SEM-EDX and XRD. The LMA elongated grains significantly enhanced ZTAs’ KIFR due to crack deflection and crack bridging mechanisms combined with transgranular and intergranular fracture modes. Additionally, higher hardness was obtained due to high LMA density, creation of low porous ZTA and strong interface bonding between LMA and ZTA grains. The KIFR was stable while the hardness was steadily declined due to more porosity accompanied by LMA *in situ* formation. Consequently, sustainable high hardness and enhanced Indentation Fracture Resistance (KIFR) of ZTA ceramics were achieved. The optimum outcomes were superior KIFR (7.8 MPa.m^1/2) and hardness (1660 HV) than the pure ZTA (5.9 MPa.m^1/2, 1568 HV). The investigation provides a new hint for future design and fabrication of economic and high performance ceramics through *in situ* formation of LMA according to the stoichiometric ratio of the reinforcing oxides.

**Keywords:**

Zirconia Toughened Alumina (ZTA); microstructure design; *in situ* formation; LaMgAl11O19 (LMA); elongated grains

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1. **Introduction**

Zirconia Toughened Alumina (ZTA) as a superior compound of Al2O3-based ceramics is a good candidate for cutting inserts, structural ceramics, and wear components. This is owing to its excellent properties such as high hot hardness, good corrosion resistance, high insulation, process flexibility, outstanding chemical and thermal stability, relatively better fracture toughness than Al2O3, as well as low cost and simple processing procedures [1,2]. Nonetheless, a number of studies have demonstrated that a good wear resistance and reliability of cutting inserts require more outstanding mechanical properties such as higher hardness besides an excellent fracture toughness [3]. Therefore, their large scale industrial usage has been significantly handicapped by this drawback. Thus, considerable attempts have been made to improve Al2O3-based ceramics’ mechanical properties, in this regard, dispersing suitable second phase reinforcements such as whiskers, fibres, ductile particles or platelets within the continuous Al2O3 matrix has been demonstrated to be a simple and viable strategy for achieving improved hardness and toughness [4]. Unfortunately, it was demonstrated that these secondary phase reinforcements were usually associated with the health hazards and required more complicated and higher cost sintering process methods like hot pressing, isostatic pressing, and colloidal processing [5–7]. Hence, a better, flexible and sustainable approach is required such as *in situ* formation of elongated grains (or particulates) of hexaluminates.

Hexaluminates or hexagonal aluminates, are the most Al2O3-rich aluminates that form, and therefore, are phase compatible with Al2O3 [8]. Since Al2O3 is the main constitute of the host matrix for ZTA, the advantageous effects of hexaluminates on the ZTA are obvious. This is related to the nature of hexaluminates’ structure and its compatibility with Al2O3. Hexaluminates are highly stable even though at high temperatures as their crystal structure is composed of spinel blocks [Al11O16]+ separated by mirror planes of layers of cations [M2+AlO3]- and O2 ions [M+O]-. Spinel blocks are composed only of Al3+ and O2- ions, having the same rigid structure as spinel [8]. The nature of these hexaluminates structures is the key parameter of their anisotropic behaviour in which high aspect ratio of grains are formed due to mismatch of thermal expansion coefficient between c-axis and a-axis of their crystals [9,10]. Hence, they are beneficial materials as they contribute to the fracture toughness enhancement due to their stability and their grain growth in various shapes such as needlike [11], platelet [7] elongated [12], rodlike [5] and flaky shapes [13]. Accordingly, these kind of grains are effectively contribute in toughness improvement of Al2O3-based ceramics through different mechanisms such as crack deflection [11,14,15], crack bridging [7,16,17] and/or combinations between them [18]. The hexaluminates are usually obtained either directly from reactions between oxides (or indirectly after calcination from carbonates, nitrates, etc.) with Al2O3 [19]. The *in situ* reaction of hexaluminates is obtained through a reaction of an oxide (or carbonate) with Al2O3 during sintering process. The *in situ* formation of hexaluminates can be efficiently used as reinforcing agent on the enhancement of mechanical properties of Al2O3-based ceramics [19]. For example, hexalumintes such as SrAl12O19, CaAl12O19, LaAl11018 and CeAl11O18 have been used for toughening of Al2O3-based ceramics. However, the hardness reduction due to their poor compactness, and therefore; porosity increment has curtailed their large scale usage [7,11,14,20,21]. Hence, to compensate such losses, the combinative reinforcing effect of multiple reinforcing agents such as multiple oxides has been actively utilised in the material design of ceramic composites [22]. Accordingly, *in situ* formation of hexaluminates obtained from various oxide additions is expected to possess a combined merits of both fracture toughness and hardness inside ceramics.

In this regard, lanthanum magnesium hexaluminate or LaMgAl11O19 (henceforth designated as LMA) is formed as the result of the stoichiometry ratio reactions between three oxides: MgO, La2O3 and Al2O3 [23]. The previous literature was proved MgO inhibits the grain growth of Al2O3 and improves its sinterability which improves the hardness significantly [1]. Additionally, La2O3 has significantly improved the fracture toughness of Al2O3-based ceramics through *in situ* formation of rodlike LaAl11018 grains [11,22,24]. However, LaAl11018 has β-Al2O3 structure which can be further improved by modifying it to the magnetoplumbite structure [8]. The major difference between β-Al2O3 structure and magnetoplumbite structure lies in the contents and arrangement of the ions within the conduction layer [25] as shown in Fig. 1. According to the study by Cinibulk [8], when the A2+ in the A2+B113+O19 is replaced by lanthanide cation, highly defective structure is produced. The ideal structure of LaAl11018 can be represented as LaO2[Al11O16]. By substituting a divalent cation for one Al3+ local charge balance is obtained. The structure now becomes LaAlO3[MAl10O16] or LMA, with the divalent cation substituting for an Al cation in the spinel block. This mechanism of charge balance leads to the ideal stoichiometric magnetoplumbite compounds LnMAl11O19, for Ln = La-Gd, and M = Mg, Mn-Zn. The magnetoplumbite structure have a chemical formula of A2+B113+O19 such as SrAl12O19 and CaAl12O19 with hexagonal structure of *P*63/*mmc* space group [26,27]. Furthermore, the separated mirror planes containing large cations cause effective suppression of grain growth along c-axis, resulting in the magnetoplumbite oxides whose plate-like hexagonal crystals have high aspect ratio [26, 28]. Besides that, the previous study done by Li and Gao [29] has investigated that the stronger bonds of LMA components which leads to high hardness of LMA (16.2 GPa or 1630 HV). Owing to the possession of high aspect ratio, excellent mechanical properties of LMA, and as the multiple oxides of MgO, La2O3 and Al2O3 are main components of LMA with different promising effects on the mechanical properties; it is expected that LMA can serve as a cost-effective and potential toughening agent to enhance fracture toughness and hardness of Al2O3-based ceramics through designing a novel microstructure [3, 4, 7]. Additionally, LMA excellent thermal properties suggests it as a potential material to be utilised as cutting inserts and for other applications that run under severe thermal conditions. In spite of these facts and widespread usage of LMA as thermal coating barrier and for luminescence applications [30–34]; there were only scarcely available reports for improvement of mechanical properties of ceramics through LMA addition. LMA has been used for toughening various Al2O3- and ZrO2-based ceramics. For example, previous studies by Tang et al. [3,4] indicated the superior fracture toughness and with just a minimal hardness drop of monolithic Al2O3 at elevated and room temperature when LMA added to the Al2O3 matrix due to LMA effect on the microstructure of Al2O3. Similarly, Gao et al. [35] have investigated the positive effect of LMA addition on the fracture toughness enhancement of 3YSZ which was related to the obtaining more excellent microstructure of 3YSZ matrix. Chen and Chen [7] work was the only investigation report of *in situ* formation of LMA inside Al2O3 matrix which reports fracture toughness improvement but accompanied with a minimal decline of hardness. However, up to date no any study on the influence of *in situ* formation of LMA inside ZTA was reported. Therefore, the aim of the current work is to design a novel microstructure of ZTA through *in situ* formation of LMA to obtain superior mechanical properties. A significant and partial improvements of the ZTAs’ fracture toughness and hardness, respectively; were investigated through *in situ* formation of LMA.

1. **Experimental Materials and Procedures** 
   1. **Materials**

The starting raw materials were Al2O3 (Martinswerk, 99% purity), YSZ (Goodfellow, 5.4% Y2O3 as stabilizer, ≥96% purity), La2O3 (III) (Aldrich, 99.99% trace metals basis) and MgO (Alfa Aesar, 99.95% metals basis). The MgO was used as a starting material instead of MgAl2O4 based on the study of Khorramirad et al. [27].

* 1. **Preparation of samples**

To form ZTA, the ratio between Al2O3/YSZ was kept at 4/1. The stoichiometry ratio was followed by the mole ratios according to the previous literature [23] to produce different ratios of LMA (1.0, 2.0, 5.0 and 9.0) wt.% inside ZTA ceramics. Prior to mixing process, the La2O3 was dried to up to 100 °C to ensure a complete evaporation of water containment of the reactive La2O3. The mixtures were wet mixed using ABB-Mixer with ZrO2 balls with weight ratio of ball to powder of 10:1. The slurries were dried for 2 days at 100 °C in an oven (Memmert-CU 9760) and the dried cakes were crushed and ground. Then the powders were hydraulically pressed by MTI pressing machine to form pellets of 18 mm in diameter and 4 mm thickness at 330 MPa for 2 minutes. The pellets were sintered for 2 hrs at 1600 °C with 5 °C/min heating rate to ensure a complete LMA formation. The furnace was switched off to cool down to room temperature.

* 1. **Characterisation**

An XRD diffractometer (Bruker AXS D2 Advance) with CuKα radiation operating at 30 kV and 10 mA was used to analyze phase compositions of the sintered samples. The scanning speed was maintained at 0.03°/s in the range of 10°≤2θ≤90°. Counting time was fixed at 38.4 s. The PANalytical X'PERT High score Plus software was used for qualitative and quantitative analyses of the XRD profiles. Field Emission Scanning electron microscopy (FESEM Ziess Supra 35 VP) attached with EDX was employed to study the microstructure and chemical composition of the samples, respectively. The density and porosity of samples containing various amount of LMA was measured using the Archimedes principle. Vickers hardness and KIFR of the sintered samples were obtained using Vickers indentation technique. The hardness tester (Mitutoyo-model HV-114) was used to measure the Vickers hardness and KIFR by taking the average of five different readings for each sample. The polished sintered samples were subjected to HV 20 kgf for 10 s.

The crack parameter measurements of crack length and half-length diagonal for the Vickers diagonal specify the crack mode, and accordingly, the method to calculate the fracture toughness. The details of such assumptions can be found elsewhere [36]. As agreed by various researchers, the Indentation Fracture (IF) toughness method (Equation 1) does not represent the true fracture toughness therefore the fracture toughness produced from IF method is termed as Indentation Fracture Resistance (KIFR) [37–39]. As a very important evidence for our work, the experimental indentation crack on Fig. 2 shows the Palmqvist crack mode. Fig. 2 was further enriched with measurements of crack lengths (l) and half length of the Vickers indentation diagonal (a) through Field Emission Electron Microscopy (FESEM, Zeiss Supra 35) based on the straight line method. The KIFR which based on fracture toughness was calculated according to the formula of Palmqvist crack proposed by Niihara:[40]

K*Ic* is the fracture toughness, H is Vickers hardness, a is the half length of Vickers diagonal (μm), E is equal to the Young modulus of the sample, and c is the length of the radial crack size (μm).

The Niihara equation measures the fracture toughness (K*Ic*). Nonetheless, Miyazaki and Yoshizawa [38] state that the KIFR value for most ceramics is roughly proportional to K*Ic,* which implies that the crack model is not very incorrect. In spite of this fact, the IF method is an acceptable method for estimation of KIFR of ceramic products and components due to its simplicity and applicability to small size of test samples [37].

1. **Results**

Fig. 3 shows the XRD diffractograms of the ZTA-LMA samples sintered for 2 hrs at 1600 °C. The main phase in all samples is Al2O3 which appeared as corundum (ICSD no. 98-003-4627) while YSZ (Zr0.96Y0.04O1.98) appeared as (ICSD no. 98-003-3611) and LMA appeared as (ICSD no. 98-001-8603). The tiny peaks of Baddeleyite (m-ZrO2, ICSD no. 98-007-1937) appeared at ZTA produced by 0.0 wt. %, 1.0 wt. % and 2.0 wt. % of LMA. However, the traces of baddelyite peaks were totally disappeared for ≥5.0 wt. % LMA samples. The Rietveld analysis confirmed minute amount of m-ZrO2. The intensity of LMA peaks has increased with higher LMA concentration while the intensity of Al2O3 peaks decreased. The YSZ remain constant due to its neutrality since it was not involved with any reaction.

The increase of LMA can be further confirmed by FESEM micrographs as shown in Fig. 4. The white YSZ grains are easily distinguishable from dark grains of Al2O3. However, the LMA grains are identified by its elongated shape which is brighter than Al2O3 grains but darker than YSZ grains. Therefore, all these three different types of compounds are easily distinguishable from each other. The number of these elongated grains increased with more *in situ* formation of LMA.

The general observation from FESEM micrographs shows a homogenous distribution of Al2O3 and YSZ grains. However, minor agglomeration of YSZ grains among Al2O3 matrix cannot be avoided [1,19]. The porosity is increased with more LMA formation. The similar phenomenon was found accompanied the *in situ* formation of hexaluminates inside Al2O3-based ceramics [3,4,12–14,41,42]. Another observation was the clustering of LMA grains together with more LMA formation. Nonetheless, it is difficult to distinguish between LMA and LaAl11O18 only by XRD and FESEM because they have the same chemical composition and space group [27]. Therefore, EDX is necessary to identify the elements of the elongated grains and their compounds.

As shown in Fig. 5, EDX can easily distinguish various grains. Fig. 5 confirms the formation of LMA inside ZTA matrix through observation of Mg approximately equals to the atomic weight of Mg portion inside LMA. Similarly, the elemental compositions of each Al2O3 and YSZ were confirmed through EDX.

Fig. 6 shows the bulk density and porosity of ZTA-LMA composites. The bulk density is continuously increased with more *in situ* LMA formation due to its higher density compared to pure ZTA. The density of LMA is (4.26 g/cm3) [31] while for the pure Al2O3 is (3.98 g/cm3) [4] and ZrO2 (6.012 g/cm3) [24]. A slight increase of density was observed with increasing *in situ* formation of LMA, from 4.14 g/cm3 for pure ZTA to 4.158 g/cm3 for ZTA-9.0 wt. % LMA. Meanwhile, only a moderate increase of porosity was recorded from 0.77% for pure ZTA to 0.883% for ZTA-9.0 wt.% LMA. This is a usual phenomenon that is usually attributed to the volumetric expansion accompanied *in situ* formation of hexaluminates [43].

Fig. 7 shows the KIFR and hardness of ZTA added with LMA samples. The KIFR is almost stable. The maximum KIFR is (7.8 MPa.m^1/2) for ZTA-1.0 wt. % LMA which is higher than the pure ZTA by 33%. Then, it slightly decreased to 7.5 MPa.m^1/2 for ZTA-9.0 wt.% LMA Despite this slight reduction, the KIFR of ZTA-LMA remains higher than that for the pure ZTA (5.9 MPa.m^1/2) by 27%. Concurrently, the Vickers hardness of ZTA-LMA ceramics is increased reaching the maximum value (1660 HV) as shown in Fig. 7. Then it maintaining a gradual downward trend with increasing LMA formation. It gradually reduced from 1660 HV for ZTA-1.0 wt. % LMA to 1551 HV for ZTA-9.0 wt. % LMA.

Fig. 8 shows the crack paths of the ZTA-LMA composites. The crack deflection and crack bridging mechanisms are visible throughout the ZTA-LMA system. Additionally, both transgranular and intergranular fracture modes were observed.

1. **Discussion**   
   The mechanical properties of ZTA ceramics are significantly affected by the microstructure and phase compositions. The LMA *in situ* formation transformed the microstructure of ZTA through creating elongated grains of the LMA, pore formation and denser microstructure compared to the pure ZTA. Therefore, this microstructure transformation has a great influences on the mechanical properties of ZTA ceramics especially in the enhancement of both hardness and KIFR. Generally, numerous studies have elucidated that distributing a small amount of elongated grains in the matrix which can effectively retard the grain growth of the matrix phases and therefore, improves the microstructure and mechanical properties of these ceramics. Nonetheless, when the amount of elongated grains exceed the optimal proportion, they tend to agglomerate or overlap together to create a fair amount of pores in the host matrix. This ultimately affects the densification process adversely, as well as mechanical properties [3].

The design of a novel microstructure through *in situ* formation of LMA has a considerable impact on the KIFR of ZTA ceramics. As shown in Fig. 8, numerous crack deflection and crack bridging mechanisms were clearly observed throughout all ZTA-LMA system. Furthermore, both intergranular and transgranular fracture modes were detected clearly for all ZTA-LMA composites. The crack deflection was obvious through the tortuous path of the cracks in ZTA-LMA samples (Fig. 8). When the crack deflected around elongated LMA grains, crack propagation is lengthened, it resulted in the consumption of the fracture energy. Consequently, the anisotropy nature of LMA effectively contributed on the enhancement of the KIFR [11,14,15]. Further strengthen of the KIFR for ZTA ceramics was achievable when the crack path was blocked by LMA elongated grains. Previous literature demonstrated that the crack bridging by elongated or platelet hexaluminate grains consumes the fracture energy which slow down the crack, and thus, improve the fracture toughness [17,44,45]. The crack bridging is frequent for all ZTA-LMA composites, and therefore, partial improvement of the KIFR is ascribed to the crack bridging effect of anisotropic LMA grains. Moreover, the transgranular fracture mode through LMA grains is another main contributor on the KIFR enhancement. This is attributable to the fact that the transgranular fracture mode has higher KIFR compared to the intergranular fracture mode due to its higher energy consumption [19] and the higher Young modulus of LMA than that for YSZ [35] while LMA Young modulus is almost identical to that of the Al2O3 matrix. The crack deflection and crack bridging combined with the transgranular and intergranular crack propagation lead to the strong toughening contributions. Hence, the KIFR of ZTA-LMA ceramics are significantly increased. The similar trend was observed through addition of LMA into Al2O3 by Tang et al. [3,4] and through *in situ* formation of LMA inside Al2O3 matrix by Chen and Chen [7]. Nonetheless, more pores observed with more in-situ formation of LMA inside ZTA ceramics as shown in SEM micrographs at Fig. 4 and porosity values at Fig. 6. The previous studies have elucidated that the pore formation accompanied hexaluminates formation during sintering process counteract the reinforcing effect of elongated or platelet hexalumintes [7,19], thereby finally leading to the slight decrease of the KIFR. Meanwhile, the phase transformation of ZrO2 has its own role on the toughening the ZTA microstructure when volume expansion occur during the cooling process and this growing volume play major role to toughen the composites [46]. Nevertheless, the XRD diffractograms at Fig. 2 shows only a tiny peaks of m-ZrO2. This indicates that the toughening portion through ZrO2 phase transformation inside ZTA matrix is much lower compared to that through *in situ* formation of LMA. The similar low contribution of ZrO2 phase transformation on toughening mechanisms was found by Kern’s work when he investigated the effect of *in situ* formation of CeAl11O18 on the properties of Al2O3-24 vol.% ZrO2 (1.4 Y) [21]. Therefore, the current work demonstrates that *in situ* formation of LMA is the superior and the major contributor of toughening ZTA composites. Consequently, LMA is highly recommendable for toughening ZTA ceramics.

The LMA *in situ* formation has a great impact on the maintaining high hardness due to higher LMA density compared to the host matrix, lower porosity of the ZTA-LMA structure compared to the *in situ* formation of other hexaluminates and a strong interface bonding between LMA grains with both Al2O3 grains and ZrO2 grains. Similar to the *in situ* formation of LMA inside ZTA, previous works by Frank [47] and Naga et al. [24] demonstrated that the *in situ* formation of LaAl11O18 assisted to create a strong interface between ZTA and LaAl11O18. The similar strong interface bonding was observed between LMA and ZTA grains as shown in the FESEM micrographs Fig. 4 (b) and (c). However, this bonding weakened with further formation of LMA elongated grains as observed in Fig. 4 (d) and (e). On the other hand, Fig. 6 demonstrates the bulk density of ZTA composites is slightly increased while the porosity variation does not go along with bulk density trend. The porosity is also steadily increased. This phenomenon is supported by SEM micrographs of Fig. 4. A small amount of interstices exist in low content of in-situ LMA formation (i.e. 1.0 wt.% and 2.0 wt.%). The amount of these interstices are moderately increased with more LMA formation. The increase of porosity is attributable to the agglomeration of LMA grains with more LMA formation, creating clusters of LMA grains and random arrangement of elongated or platelet grains of LMA [48]. The elongated nature of these grains facilitate the interlocking them when they impinge each other. Therefore, numerous pores trapped between them. These pores act as stress concentrators and counteract the reinforcing effect of hexaluminate grains, finally leading to the decrease of hardness [3]. This implies that appropriate amount of LMA platelets is beneficial for the densification process of Al2O3-based ceramics. However, when the amount of platelets exceeds the critical value, the platelets may stack or overlap mutually, thereby impairing the densification kinetics to attain dense ceramics [4]. The density values of various ZTA-LMA composites is the mirror image of this fact. The *in situ* formation of LMA more than 2.0 wt.%, maintains a tiny increment of bulk density and keeps its values around 4.15 g/cm3. As it was evident from FESEM micrographs of Fig. 4, the bonding interface between Al2O3 and LMA grains was weaker when the amount LMA inside ZTA exceeds the critical portion (2.0 wt.% LMA). Accordingly, the hardness is moderately decreased from the maximum value (1660 HV for 2.0 wt.% LMA) to only 1551 HV for ZTA-9.0 wt.% LMA (6.5% reduction). This trend is quite similar to the outcome achieved by Tang et al. [4]. This suggests that the *in situ* formation of LMA inside Al2O3-based ceramics is able to maintain acceptable hardness compared to the disastrous drop of hardness obtained from the *in situ* formation of other hexaluminates. Moreover, this investigation supports the hypothesis of superior LMA over LaAl12O18. The vacancies between mirror planes will be filled by Mg and this effectively gives harder structure for the ZTA ceramics.

It is evident from the previous details that the *in situ* formation of 2.0 wt.% LMA inside ZTA is the optimal to enhance mechanical properties. Further LMA formation deteriorates the hardness, and relatively the KIFR of ZTA ceramics. This optimum portion of LMA contributes in mechanical improvement mainly through elongated grains nature by providing both crack deflection and crack bridging mechanism with relatively little pore formation. Consequently, the LMA is highly recommended for enhancement of mechanical properties of ZTA.

1. **Conclusions**

The design of a novel microstructure through *in situ* formation of LMA inside ZTA ceramics has successfully enhanced its KIFR and hardness. Crack deflection and crack bridging combined with transgranular and intergranular crack propagation are major contributors to the toughening of ZTA ceramics. These contributors were mainly governed by LMA due to its elongated anisotropic feature while further increase of LMA formation inside ZTA ceramics accompanied with creation of a little pores which results in minor decrease of KIFR. Therefore, the maximum KIFR was 7.8 MPa.m^1/2 was found to be 33% higher than that for pure ZTA (5.9 MPa.m^1/2). *In situ* formation of LMA also successfully produced harder ZTA ceramics (maximum at 1660 HV) due to its higher density than ZTA, strong interface between LMA and ZTA grains and relatively low porous microstructure. The investigation demonstrates that the design of a novel microstructure of ZTA ceramics through *in situ* formation of LMA based on the stoichiometric ratio of the reinforcing oxides is a very efficient approach to improve the overall mechanical properties of ZTA ceramics.

**Acknowledgements**

This work is financially supported by research university grant, Universiti Sains Malaysia (USM) RUI 1001/PBAHAN/80140876 and teaching fellow scheme USM. 9/25 Jld. XIII. The authors are grateful for Mr. Muhammad Khairi Khalid for his assistance of FESEM tests.

**Conflict of interest**

The authors declare that they have no conflict of interest.

**Data availability**

• The raw/processed data required to reproduce these ﬁndings cannot be shared at this time due to technical or time limitations.

• The raw/processed data required to reproduce these ﬁndings cannot be shared at this time as the data also forms part of an ongoing study

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