Effect of LZSA glass-ceramic addition on the erosive wear of pressureless sintered alumina

Abstract

This study aims to evaluate the influence of the 11.6Li₂O-16.8ZrO₂-68.2SiO₂-3.4Al₂O₃ (mol%) glass-ceramic addition (LZSA, 7 to 21 vol%) on the erosive wear of alumina in comparison to values of pure alumina obtained from the literature. Thus, composites were prepared from three commercial alumina of different initial particle sizes. Specimens were obtained by uniaxial pressing. Sintering temperatures and holding times were found to be different for each composite. The erosive wear test was carried out in an apparatus based on the standard ASTM G76-4. The volumetric erosive wear ($T_{vol}$) was correlated to the initial mean particle size of alumina, LZSA glass-ceramic content, average grain size of sintered alumina (AGS), porosity (P), elastic modulus, fracture toughness, natural defect size, and fracture energy based on a correlation matrix of statistical analyses. The experimental data of $T_{vol}$ fit very well with P and AGS, individually, in a 3rd degree equation, except for composite A₂₁. Composite A₂₁, i.e. 21 vol% LZSA added to 0.5 µm mean particle size alumina (AF, fine alumina) and sintered at 1470 °C for 3 h, showed interesting results of $T_{vol}$ (2.05 × 10⁻⁸ m³·kg⁻¹) related to the other investigated compositions, which varied from 1.90–4.37 × 10⁻⁸ m³·kg⁻¹, and those existing in literature (0.55 × 10⁻⁸ to 10.78 × 10⁻⁸ m³·kg⁻¹), mostly when considering the lower sintering temperature (1470 against 1600 °C). Thus, although the AC₇ composite had shown the lowest $T_{vol}$ value (1.90 × 10⁻⁸ at 1600 °C/7 h), the composite A₂₁ can be considered as the best result because of its lower sintering temperature and holding time (2.05 × 10⁻⁸ at 1470 °C/4 h). The formation of a viscous liquid phase, which crystallizes during the controlled cooling in the microstructure of the LZSA/alumina-based composites, improves the erosive wear of the alumina.

Keywords: alumina; LZSA glass-ceramic; composites; erosive wear.

1. Introduction

The oil exploration and production in ultra-deep water presents numerous technological challenges to be overcome. The pre-salt layer in Brazil, for example, has a 7 000 m water depth. One of the technological bottlenecks is in the material used to transport oil and gas from its source to the production platform. The material needs to have high wear resistance because solid particles are conveyed along with the fluid and cause degradation by erosion of the
inner lining of the pipe (or risers) and valves (Milak, 2015).

Numerous industrial components are subject to erosive and abrasive wear on this conveyor system. Valves can be considered as critical points, as the free area to the transport of the fluid is reduced at these points, increasing the fluid velocity and the wear in these regions. Due to the extensive water depth, where wellhead equipment and valves are located, the access to maintenance is restricted. This entails a high cost of replacing this component. Thus, it is necessary that the valves have low wear and consequently, long service life (Milak, 2015).

Alumina is a typical engineering material (Medvedovski, 2001; Cesari et al., 2006; Kumar et al., 2006; Medvedovski, 2006; Puchy et al., 2013; Silva et al., 2014; Milak et al., 2015) that can meet several engineering requirements (Medvedovski, 2001) for many applications, such as structural (Medvedovski, 2006), automotive, aerospace, biomedical, ballistic (Silva et al., 2014) and as cutting tools (Kumar et al., 2006). Moreover, the use of alumina in wear applications plays an important role. An important review of wear performance of alumina-based ceramics was published by Milak et al. (2015).

One may define wear as being a dynamical process that results from mechanical interaction between different bodies, a solid and another solid or fluid. Changes in the surfaces occur because of the relative movement between the bodies (Williams, 2005). Several factors and parameters may interfere in this process, such as the geometry of the contacting surfaces, applied normal force, relative velocity, and properties of the materials, among others (Ashraf et al., 2009).

Wear is affected by the interaction (contact mode) between of abrasive particles and material surface, besides the properties of the involved materials (Pavelescu and Musat, 1974). In relation to the involved materials, composition, hardness, fracture toughness, and grain size assume an important role.

Erosive wear is one of the wear modes that is caused by solid particles transported by a fluid, which collide with each other and cause damage on the surface under wear (Kuzmenko, 1981). Erosion can be considered as a continuous mass reduction of a material caused by the action of a wear material upon the surface, as related in the ASTM G 40-92. In ceramic materials, which exhibit brittle behavior, the formation of cracks and microcracks plays an important role, causing the removal of eroded material to occur through the interconnection of cracks (Ball, 1986).

The influence of the grain size on the mechanical behavior of alumina has been focused on in the last decades (Cho et al., 1989; Mukhopadhyay and Mai, 1993). Moreover, conditions of sintering that make feasible the densification without significant grain growth are suitable for the microstructural refinement. Such behavior may be observed in other wear modes (Miranda-Martinez et al., 1994).

The wear mechanism of brittle materials at angles close to 90° is due to the fatigue of the intergranular phase, followed by microcracks in the grain boundary, induction of microcracks in the grain and their subsequent detachment (Marques, 2006).

Different strategies are available to improve the erosive wear of alumina (Milak et al., 2015). For example, Montedo et al. (2015) have investigated the effect of a LZSA 11.6Li₂O-16.8ZrO₂-68.2SiO₂-3.4Al₂O₃ (mol%) glass-ceramic addition on the sintering behavior of alumina. The results showed that LZSA glass-ceramic increased the densification of the studied alumina, reducing the sintering temperature. Because of this, a suppression on the grain growth occurred. Elongated grains were also observed. They concluded that the addition of such glass-ceramic could be used to improve the densification of alumina for the potential application in wear-resistant materials. We hypothesize that an improvement on the mechanical properties could occur due to the addition of LZSA glass ceramic to alumina in such way to increase the erosive wear resistance of the alumina.

In fact, previous works (Montedo et al., 2017; Montedo et al., 2018) investigated the addition of 21 vol% of a 11.6Li₂O-16.8ZrO₂-68.2SiO₂-3.4Al₂O₃ (mol%) glass-ceramic to a fine grain alumina, sintered at 1470°C and 3 h holding time (2% porosity). They observed that the glass-ceramic addition caused a much more significant effect on the mechanical properties than the initial particle size of alumina. This composition showed a fracture toughness of 4.93 MPa·m⁰.5, elastic modulus of 210 GPa, fracture energy of 57 J·m⁻² and flexural strength of 170 MPa. They concluded that the use of the LZSA glass-ceramic allowed to significantly modify the microstructure of alumina, and consequently, its mechanical properties.

Considering these works (Montedo et al., 2017; Montedo et al., 2018) involving the addition of a LZSA glass-ceramic to a fine grain alumina, we hypothesize that such composite could present a lower wear rate related to pure alumina, refining the microstructure and improving the erosive wear resistance of alumina.

Thus, this article aims to evaluate the effect of the addition of LZSA glass-ceramic on the erosive wear of alumina, in comparison to values of pure alumina obtained from literature, whereby plates of LZSA glass-ceramic/alumina composites could be used for the inner lining of valves existing in oil transportation systems, increasing their lifespan.

2. Materials and methods

2.1 Materials

LZSA glass-ceramic composition (Tecnofrita, Brazil) and three alumina (99.8 wt% of Al₂O₃, Almatis, USA) were used in this study (Table 1). Chemical composition was determined by X-ray fluorescence spectrometry (Panalytical, model Axios Max, United Kingdom), and atomic absorption spectrometer UNICAM, model SOLAR 969, United Kingdom), particle size in a particle size analyzer (CILAS 1064, France) and specific surface area by BET method (Micromeritics ASAP 2020, USA). LZSA glass-ceramic composition shows high Na₂O and B₂O₃ contents, respectively 3.7 and 4.6 wt% of Na₂O and B₂O₃ are flux agents and were used to decrease the sintering temperature (Montedo et al., 2015). More than an energetic gain, the main objective was to avoid the excessive growing of alumina grain (Montedo et al., 2017; Montedo et al., 2018) although this addition promotes an increase of the residual glassy phase, which causes damage to the mechanical properties.
Table 1 - Chemical composition (wt%) and physical properties of the used materials.

| Oxides          | A 16 SG (fine alumina) | A 15 SG (average alumina) | A 3500 SG (coarse alumina) | LZSA |
|-----------------|------------------------|---------------------------|-----------------------------|------|
| Al₂O₃           | 99.8                   | 99.8                      | 99.8                        | 6.63 |
| Na₂O            | 0.07                   | 0.07                      | 0.07                        | 3.74 |
| Fe₂O₃           | 0.02                   | 0.02                      | 0.02                        | 0.25 |
| MgO             | 0.05                   | 0.04                      | <0.01                       | 0.00 |
| SiO₂            | 0.03                   | 0.02                      | 0.02                        | 65.15|
| CaO             | 0.02                   | 0.03                      | 0.03                        | 0.13 |
| B₂O₃            | <0.01                  | <0.01                     | <0.01                       | 4.57 |
| K₂O             | 0.00                   | 0.00                      | 0.00                        | 0.82 |
| TiO₂            | 0.00                   | 0.00                      | 0.00                        | 0.06 |
| Li₂O            | 0.00                   | 0.00                      | 0.00                        | 8.75 |
| ZrO₂ + HfO₂     | 0.00                   | 0.00                      | 0.00                        | 0.41 |
| Others          | 0.00                   | 0.00                      | 0.00                        | 0.51 |

Physical properties

- Specific surface area (m²·g⁻¹): 8.9, 4.9, 1.9, 8.36
- d₅₀ (µm): 0.5, 1.7, 2.8, 1.42

Table 2 - Experimental design with the combinations among each factor.

| Material code | d₅₀ (µm) of alumina | LZSA (vol%) | Sintering conditions |
|---------------|---------------------|-------------|----------------------|
|               | (µm) of alumina    | (wt%)       | T (ºC) | t (h) |
| A₇            | 0.5                 | 7           | 1600 | 4    |
| A₁₅           | 1.7                 | 15          | 1600 | 3    |
| A₂₁           | 0.5                 | 21          | 1470 | 3    |
| A₂₁           | 2.8                 | 21          | 1600 | 0.67 |

2.2 Experimental design

Table 2 shows the experimental design used in this study. Two factors (initial mean particle size of alumina and glass-ceramic content) and two levels (-1 and +1) were considered, representing a full factorial design 2² with a central point. The experimental conditions of the central point were repeated (three specimens) to increase the statistical reliability of results.

The description Aᵢ is related to the initial mean particle size of alumina, where Aᵢ is the fine alumina, Aᵢ is the average alumina and Aᵢ is the coarse alumina. The number next to this description refers to the glass-ceramic content. The composition Aᵢ₁₅ refers to the center point and was used in triplicate. The same experimental design was also used in previous studies (Montedo et al., 2017; Montedo et al., 2018). Thus, results of these studies, especially porosity and average grain size, are going to be used to understand the results obtained presented herein.

2.3 Composites Processing

Compositions were wet-mixed using 0.1 wt% sodium tripolyphosphate as dispersant, 1 wt% carboxymethylcellulose as plastifier and 1.5 wt% polyvinyl alcohol as binder. These amounts of the additives were experimentally determined. Suspensions were dried in a spray-dryer (LabMaq do Brasil Ltda LM MSD 1.0, Brazil) to obtain powders containing 8 wt% water. Subsequently, such powders were pressed by uniaxial pressing (Gabrielli GT 0785, Italy; 128 MPa specific pressure). Green densities ranging from 1920 to 2610 kg·m⁻³ were obtained, depending on the LZSA content. Specimens were dried at 110 ±5 ºC in a laboratory oven.

Because of the effect of LZSA glass-ceramic on alumina densification, the sintering temperature and holding time cannot be set. Thus, sintering temperatures (Montedo et al., 2015) were determined in an optical dilatometer (Expert System Solutions S.R.L Misura HSM ODHT 1400, Italy; 1 ºC·min⁻¹ heating rate, 90 min holding time at 1100 and 1300 ºC, 1600 ºC maximum temperature at different holding times, depending on the composition, and natural cooling up to room temperature). The criteria used to define the sintering temperature and holding time was the maximum linear shrinkage achieved for each composite. Table 2 shows the sintering conditions (temperatures and holding times) used in this study. Specimens were sintered in an electrical kiln (Fortelab ME 1700/10, Brazil). Cooling was controlled (10 ºC·min⁻¹ heating rate, 30 min...
holding time at 760 ºC, 10 ºC·min⁻¹ heating rate up to room temperature) to crystallize the glass and improve mechanical properties as related by Montedo et al. (2018).

### 2.4 Characterization of the sintered composites

Porosities were calculated from values of relative density published by Montedo et al. (2017).

The erosive wear test was carried out in an apparatus described by Vicenzi, and Marques (2011) and based on the standard ASTM G 76-4 (Standard Test Method for Conducting Erosion Tests by Solid Particle Impingement Using Gas Jets). The sample holder is fixed inside the furnace by a rod coupled to a bearing system, which allows the sample holder to be rotated between 10 and 90°, allowing to study the erosion according to the erosive particle incidence. A thermocouple is inserted into the underside of the sample holder and is held in contact with the eroded test specimen. The apparatus allows the test to be carried out up to 1000 ºC. However, erosive tests were carried out at 130 ºC, because such temperature is higher than the one found in several applications, such as the transport of oil during extraction in deepwater. The impact angle interferes on the wear according to the nature of the material tested. For brittle materials, the used impact angle is 90°. A 370 µm average particle diameter alumina was used as erodent material and 50 m·s⁻¹ was the velocity.

Based on the erosion test, the volumetric erosive wear is calculated from the measurements of the mass loss of each composition according to Equation (1):

\[
T_{\text{vol}} = \frac{(m_i - m_f)}{d_{\text{bulk}} * m_e}
\]

where \(T_{\text{vol}}\) is the volumetric erosive wear (m³·kg⁻¹), \(m_i\) is the initial mass of the specimen (kg), \(m_f\) is the final mass of the specimen (kg), \(d_{\text{bulk}}\) is the density of the eroded material, and \(m_e\) is the mass of the erodent (kg).

The results of \(T_{\text{vol}}\) obtained for the sintered composites investigated in this study were compared to those studied by Bergmann et al. (2011). In his research, Bergmann et al. (2011) used two alumina provided by Alcoa: APC 2011 (\(d_{50} = 1.5\) µm) and A-2G (\(d_{50} = 2.2\) µm). Bergmann et al. (2011) investigated such alumina pure and with the addition of a soda-lime glass. For alumina APC 2011, Bergmann et al. (2011) tested compositions containing 0 and 1 wt% of soda-lime glass, while for alumina A-2G, the soda-lime glass contents were 0, 2, 4, and 8 wt%.

The microstructure of the specimens was evaluated by scanning electron microscopy (Zeiss EVO MA10, England). The average grain size of the sintered compositions was determined by using the line-intercept method with at least 50 intercepts for each analyzed image (at least 200 measurements) (Callister, 2007).

### 3. Results and discussion

Wear is a very complex process, since many factors interfere in such phenomenon, such as average grain size and porosity. In our study, a new factor was added to the analysis: the addition of the LZSA glass-ceramic. As related in previous works (Montedo et al., 2017; Montedo et al., 2018), the addition of the precursor of LZSA glass-ceramic to alumina reduces the sintering temperature and favors the densification, while during controlled cooling, this forms crystalline phases that improve some mechanical properties. The hypothesis to be investigated would be “could the improvement in such mechanical properties reduce the erosive wear of alumina?”. The synergy in these factors increases such complexity. Because of this, a wider investigation needs to be done for a better understanding of the erosive wear in the investigated composites, as will be further demonstrated. However, this study aims to improve the understanding of the effect of such addition.

For this, we used three alumina, with different initial mean particle size, and three LZSA glass-ceramic contents, according to Table 2. However, each alumina densifies at a different sintering temperature, according to the recommendation of the supplier. Moreover, each LZSA content added to alumina requires different sintering conditions (temperature and holding time) to densify the investigated composites leading to different microstructures, typically different porosities, average grain size and even form of the particles. We are going to try making a relationship between each investigated factor and the erosive wear.

Table 3 shows the volumetric erosive wear \(T_{\text{vol}}\) in function of the LZSA content and initial mean particle size of alumina. Initially, it seems that the interaction between the LZSA content and initial mean particle size of alumina should be considered, since \(T_{\text{vol}}\) increases with the increase of LZSA content and the increase of initial mean particle size of alumina, in the investigation range of this study, ranged from composition \(A_{7.7}\) (7 vol% of LZSA and 0.5 µm initial mean particle size) to composition \(A_{21.5}\) (21 vol% of LZSA and 2.8 µm initial mean particle size).

| LZSA content (VC), m³/m³ | Volumetric erosive wear (Tvol), m³·kg⁻¹ |
|-------------------------|----------------------------------------|
|                         | \(d_{50} = 0.5\) µm                  | \(d_{50} = 1.7\) µm                  | \(d_{50} = 2.8\) µm                  |
| 7                       | \(2.33 \times 10^6\)                 | \(3.73 \times 10^4\)                 | \(1.90 \times 10^6\)                 |
| 15                      | \(2.05 \times 10^6\)                 | \(3.73 \times 10^4\)                 | \(4.37 \times 10^6\)                 |
| 21                      | \(2.05 \times 10^6\)                 | \(3.73 \times 10^4\)                 | \(4.37 \times 10^6\)                 |
On the other hand, compositions $\text{A}_7$ (7 vol% of LZSA and 2.8 µm initial mean particle size) and $\text{A}_{21}$ (21 vol% of LZSA and 0.3 µm initial mean particle size) do not follow such behavior. Thus, considering data of Table 3, one cannot establish a direct correlation between $T_{\text{vol}}$ and the unique investigated factor.

Taking into account the complexity of the involved phenomena, we are going to evaluate the effect of the different factors on the erosive wear. Although the involved phenomena show higher complexity, for simplicity, we carried out the evaluation in four different levels:

i) $N_1$: manipulated variables (d$_{\text{ag}}$ of alumina – D50, and LZSA glass-ceramic content – VC);

ii) $N_2$: properties of the resultant microstructure (average grain size of sintered alumina – AGS and porosity – P);

iii) $N_3$: mechanical properties of the sintered composites (elastic modulus – E, fracture toughness – KIC, natural defect size – a, and fracture energy – γ). These properties were obtained from Montedo et al. (2018);

iv) $N_4$: dependent variable (volumetric erosive wear – $T_{\text{vol}}$).

Thus, experimental data from this study and Montedo et al. (2018) related to the same samples will be considered. Table 4 summarizes such experimental data.

Table 4 - Mechanical properties and porosities of the studied composites.

| Composite | Sintering conditions | P* (%) | E (GPa) | $K_{\text{C}}$ (MPa·m$^{0.5}$) | γ* (J·m$^{-2}$) | a* (µm) | AGS (µm) |
|-----------|----------------------|--------|---------|----------------------------|----------------|--------|--------|
| $\text{A}_7$ | 1600 °C/4 h | 1.2 | 298 | 4.24 | 30.2 | 71 | 15.05 |
| $\text{A}_7$ | 1600 °C/7 h | 1.8 | 295 | 3.90 | 25.8 | 170 | 16.14 |
| $\text{A}_{15}$ | 1600 °C/3 h | 3.8 | 252 | 4.31 | 36.9 | 136 | 7.22 |
| $\text{A}_{21}$ | 1470 °C/3 h | 4.3 | 222 | 4.93 | 54.8 | 241 | 5.81 |
| $\text{A}_{21}$ | 1600 °C/0.67 h | 5.4 | 215 | 4.60 | 49.3 | 231 | 6.25 |

* calculated.

First of all, we are going to exclude composite $\text{A}_{21}$ of this evaluation. Such composition will be analyzed further because it densifies at a lower temperature (Table 2) with important consequences in the involved phenomena.

We made a statistical analysis of the data of Table 4. Table 5 shows the correlation matrix of the evaluated factors.

Table 5 - Correlation matrix of the evaluated factors.

| Factors | VC | D50 | AGS | P* | E | KIC | γ* | a* | $T_{\text{vol}}$ |
|---------|----|-----|-----|----|---|-----|-----|----|--------------|
| VC | 1.00 |         |     |     |   |     |     |    |              |
| D50 | 0.44 | 1.00 |     |     |   |     |     |    |              |
| AGS | -0.95 | -0.27 | 1.00 |     |   |     |     |    |              |
| P* | 0.99 | -0.94 | 1.00 |     |   |     |     |    |              |
| E | -1.00 | -0.48 | 0.94 | -0.99 | 1.00 |     |     |    |              |
| $K_{\text{C}}$ | 0.87 | 0.00 | -0.84 | 0.80 | -0.86 | 1.00 |     |    |              |
| γ* | 0.92 | 0.19 | -1.00 | 0.90 | -0.91 | 0.83 | 1.00 |    |              |
| a* | 0.72 | 0.93 | -0.53 | 0.78 | -0.74 | 0.37 | 0.45 | 1.00 |              |
| $T_{\text{vol}}$ | 0.98 | 0.27 | -0.99 | 0.95 | -0.97 | 0.91 | 0.97 | 0.56 | 1.00 |

In Table 5, the higher the value of the factor (in modulus), the higher the statistical correlation between the evaluated factors; positive values mean direct effect, i.e. both analyzed factors increase in relation to each other, and for negative values, an increase of the analyzed factor implies in the decrease of the another one. One may see in Table 5 that $T_{\text{vol}}$ is strongly correlated with VC (0.98) in the variation range of the evaluated factors. The higher the VC, the higher the $T_{\text{vol}}$.

As pointed out by Montedo et al. (2017), the increase in the LZSA glass-ceramic addition content (VC) reduces the elastic modulus for two main reasons: the increase of the porosity and the reduction of the higher elastic modulus phase – α-alumina. The α-alumina is also the harder phase of the composite; therefore, an increase in $T_{\text{vol}}$ is expected with the reduction of the α-alumina content. On the other hand, $T_{\text{vol}}$ is weakly correlated with D50 (0.27).

According to the factors related to the second level, $N_2$, one may observe that $T_{\text{vol}}$ is strongly correlated with AGS (-0.99) and P (0.95) but in an opposite way. The higher the AGS, the lower the P, and consequently, the lower the $T_{\text{vol}}$. Since these two factors showed high correlation with $T_{\text{vol}}$, a better analysis is required.

Figure 1 shows porosity (P) and average grain size of alumina (AGS) in function of the volumetric erosive wear ($T_{\text{vol}}$). In this figure, the isolated experimental data represent the composite $\text{A}_{21}$. Higher porosity means less contact points (lower anchoring of the particles) and higher susceptibility to the pull-off of the alumina particles. Zhou and Bahadur (1995) observed this erosive wear mechanism in fragile materials.
The porosity and AGS of the sintered samples interfere directly on the $T_{vol}$ behavior. $T_{vol}$ increases with the P increasing, because $K_{IC}$ and $E$ decrease with the decrease of AGS. The composite $A_7$ showed in practice the same $T_{vol}$ value as $A_7$ probably because they show almost the same porosity and AGS values. Although $A_7$ presents the highest D50, the LZSA addition caused the suppression of alumina grain growth (Montedo et al., 2017). On the other hand, the composition $A_21$, although containing higher VC than $A_7$ and lower D50 than $A_7$, showed in practice the same Tvol value. It seems that the interaction between AGS and P also interferes directly in the $T_{vol}$ behavior. In such case, the higher porosity (4.3 vol%) of $A_21$, in relation to $A_7$ and $A_7$, would increase $T_{vol}$ since there is damage to the mechanical properties. On the other hand, the lower AGS (5.81 µm), in relation to $A_7$ and $A_7$, could decrease $T_{vol}$. It seems that higher wear mass occurs at higher D50, i.e. in relation to a smaller particle size of alumina, a larger one once removed from the material would increase the wear mass. Thus, there could be a “compensation” into the effect of those two factors on $T_{vol}$. The level of importance of each one should be investigated.

However, in the case of composite $A_21$, it is also possible that the reason for its low $T_{vol}$ can be related to the higher residual compressive stress in relation to the other composites, as discussed by Montedo et al. (2018), at lower sintering temperature and holding time ($1470 \, ^\circ C/4 \, h$). Compressive residual stresses can be formed in the composites during controlled cooling because of the difference in the coefficients of thermal expansion (CTE) between the glass-ceramic and alumina, interfering in the fixation of the alumina particles during the erosive tests. In such case, the interaction between the alumina particles and the glass-ceramic would assume an important role. In addition to this, the phases formed in the grain boundary and the microstructure show a fundamental importance on the wear (Goswami and Das, 2000; Švanárek et al., 2011), as verified by Montedo et al. (2018). Therefore, the residual compressive stress generated by the LZSA glass-ceramic added to alumina in the composite $A_21$ promotes the increase of $K_{IC}$ (4.93 MPa-m$^0.5$) and $\gamma$ (54.8 J·m$^-2$), compared to the other investigated composites, despite its high porosity.

Although porosity has increased with the increasing of glass-ceramic content, the increase of $K_{IC}$ (due to increased alumina-LZSA interaction) reduced erosive wear as predicted by Wellman and Allen (1995). Thus, it is possible that the lower specific surface area of the $A_21$ (lower AGS) associated with higher LZSA content causes the occurrence of residual compressive stress, promoting stronger LZSA/alumina interface, causing the increase in $K_{IC}$ and $\gamma$, and hence reducing Tvol. Such specific behavior was not observed in the other composites. It is possible that $\alpha$-alumina nanoparticles reinforced with 21 vol% LZSA (or more) can still present lower $T_{vol}$.

Table 5 also shows that $T_{vol}$ is strongly correlated with elastic modulus (higher $E$, lower $T_{vol}$) and with fracture energy (higher $\gamma$, higher $T_{vol}$), and is weakly correlated with natural defect (a). The dependence of $T_{vol}$ on $E$ is expected. Apparently, the effect of $\gamma$ on $T_{vol}$ is contrary to what might be expected. This deserves special attention because after all, alumina-LZSA system increases the fracture energy. On the other hand, this increase did not promote the increase in wear resistance in most cases. The experimental datum that was left out to constitute the correlation matrix, composite $A_21$, proves that even a higher LZSA glass-ceramic content can present higher wear resistance (low $T_{vol}$), since it shows the highest fracture energy value among the evaluated composites. Moreover, composite $A_21$ presents the lowest AGS. Thus, the behavior of composite $A_21$ probably occurred by the association of three factors: smaller initial mean particle size, higher LZSA content, and lower sintering temperature.

The addition of the LZSA glass-ceramic modified the form of the alumina particles (Figure 2), which should significantly interfere in the mechanical behavior.

Figure 2 shows that elongated alumina was obtained regardless the LZSA content and the initial mean alumina particle size. The elongated alumina grains can reinforce the microstructure, increasing $K_{IC}$ (Goswami and Das, 2000; Goswami et al., 2000). One can consider that the presence of crystals formed from the parent glass after controlled cooling, i.e. the formation of the LZSA glass-ceramic, assumes an important role about the particles these impact on the material. This is because of the smaller
modulus of elasticity of the glass-ceramics than the one of alumina. Therefore, this second phase could transform part of the energy received during the erodent shock in elastic deformation, without concentrating stresses in the defects, such as cracks and microcracks, associated or not to the pores of the material, which could reduce the interferences on the erosive impact on the tested material. This means that the addition of LZSA glass-ceramic in alumina could modify the ceramic wear mechanism.

Bergmann et al. (2011) investigated the erosive wear using two commercial alumina (APC 2011, d_{50} = 1.5 µm, and A-2G, d_{50} = 2.2 µm) and a soda-lime glass as an additive to form a liquid phase during sintering. Bergmann et al. (2011) achieved T_{vol} values ranging from 0.55 × 10^{-8} to 10.78 × 10^{-8} m³·kg⁻¹.

Accordingly, the introduction of a glass that forms a liquid phase during sintering and crystallizes during cooling, to the microstructure of ceramic bodies based on alumina, allows further investigation of the relationship between microstructure and erosive wear.

Thus, the combination of good mechanical properties, with the addition of low glass-ceramic content, results in lower wear rates for the investigated compositions.

Figure 2 - SEM images of the investigated composites.

4. Conclusions

The influence of 11.6Li₂O·16.8ZrO₂·68.2SiO₂·3.4Al₂O₃ (mol%) glass-ceramic addition on the erosive wear of alumina was investigated, in comparison to values of pure alumina obtained from literature. Taking into account the complexity of this phenomena, a statistical analysis was carried out considering four different factors: manipulated variables (d_{50} of alumina – D50, and LZSA glass-ceramic content – VC); properties of the resultant microstructure (average grain size of sintered alumina – AGS and porosity – P); mechanical properties of the sintered composites (elastic modulus – E, fracture toughness – K_{IC}, natural defect size – a, and fracture energy − γ); and dependent variable (volumetric erosive wear – T_{vol}).

The statistical analyses demonstrated that T_{vol} is strongly correlated to VC, AGS, P, E, K_{IC}, and γ. Such analyses showed that T_{vol} increases with the increase of VC, P, KIC, and γ, and with the decrease of AGS and E. A specific evaluation was carried out considering the effect of porosity and average grain size of sintered alumina on T_{vol}. The composite A₂1, i.e. 21 vol% LZSA added to 0.3 µm mean alumina particle size (AF, fine alumina) and sintered at 1470 °C for 3 h, showed an interesting value of T_{vol} (2.05 × 10^{-8} m³·kg⁻¹) related to the other investigated compositions, if considering the lower sintering temperature and holding time (1470 °C/4 h). The reason for its low Tvol can be related to the higher residual compressive stress in
Effect of LZSA glass-ceramic addition on the erosive wear of pressureless sintered alumina

(below AGS) associated with higher LZSA content causes the occurrence of residual compressive stress, promoting a stronger LZSA/alumina interface, causing the increase in $K_c$ and $\gamma$. Such specific behavior was not observed in the other composites. It is possible that $\alpha$-alumina nanoparticles reinforced with 21 vol% LZSA (or more) can present an even lower $T_{cr}$. Accordingly, the formation of a viscous liquid phase, which crystallizes during the controlled cooling, in the microstructure of the LZSA/alumina-based composites, improves the erosive wear of the alumina.

Acknowledgements

Authors are very grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq/Brazil, Processes n. 308669/2016-9 and n. 550178/2012-0) and Financiadora de Estudos e Projetos (FINEP/Brazil, agreement n. 1981/10) for supporting this study.

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Received: 13 March 2019 - Accepted: 31 October 2019.