CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2024, Vol. 18, No. 1, pp. 1–6

Chemistry

STRENGTHENING OF MULLITE CERAMICS WITH SILVER REINFORCEMENTS

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https://doi.org/10.23939/chcht18.01.001

Abstract. Mullite-based composites reinforced with silver particles were obtained by powder techniques. Composites were sintered after an intense mixing of the precursor powders. It was found that additions of silver have a strong effect on the mechanical properties, since fracture toughness was increased up to 350 %. The microstructure of composites presents grains with flakes morphology.

Keywords: mullite, ceramic composites, silver reinforcements, fracture toughness.

1. Introduction

Alumina-based composites reinforced with a great diversity of materials (ceramic and metallic) have been studied extensively.[1] All these alumina-based composites have been obtained by a wide variety of processes such as: reactive metal penetration, sol gel, hot pressing of powders obtained by chemical routes, powder techniques, co-extrusion, slip casting and even through the approach of machine learning.[1-4] Some of these studies generally have shown that the homogeneous incorporation of particles of ductile metals in the ceramic matrix, can made toughen the ceramic composite resulting.[5-9] In these studies, they have concluded that when metallic particles are added to the ceramics in addition to the fine size of the particles and their homogeneous distribution in the matrix, the main mechanism of reinforcement is the crack bridging caused by the presence of these metallic particles.[1]

Instead, an alternative ceramic material added to alumina is the mullite ($3Al_2O_3{\cdot}2SiO_2$), which is an aluminosilicate having refractory applications due to its high melting point (2123 K) and excellent creep resistance. Likewise, the mullite-based ceramics have favorable properties, for instance good mechanical resistance, chemical and thermal stability, and above all they can preserve most of their mechanical behavior at high temperatures.[9-10] However, its applications as a structural material has been limited due to its high brittleness; that is, it is not easily deformed under the action of a load due to its high elastic modulus values. Due to this peculiarity, the mullite-based ceramics are sensitive to minimal imperfections in their microstructure, which act as stress concentrators that can initiate cracks causing their rapid fracture under the action of minimum stresses.[11]

Mullite-based composites reinforced with other ceramics such as ZrO_2, cordierite, Cr_2O_3 and with metals such as Co, Cu, Ni and Ti[12-14] have also been studied. For these composites conventional powder techniques have been used for their production. These studies indicate that metals as reinforcing agents provide better mechanical properties than reinforcing ceramics.

Few studies were found in the literature on the reinforcement of mulite by metals and only one research studied silver as a reinforcing medium.[15] For this reason and due to the high ductility of Ag allowing its usage as the reinforcing material, in this study we propose the processing of a new type of composite material based on mullite reinforced with silver particles.

2. Experimental

For the preparation of the mullite/Ag composites, we used mullite powders (Dillwyn Virginia USA, 99.9 % purity and 1-micron particle size) and silver (Sigma-Aldrich, 99.5 % purity and 100 nm particle size). The

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silver was added to the mullite in the amount of 0.0, 0.5, 1, 2 and 3 wt. %. Once the powder mixtures were weighed, they were separately ground for 3 h at 300 rpm in a planetary type mill (Retsch, Germany, PM100), using 3 mm diameter ZrO_2 spheres as grinding elements, with 12:1 (w/w) ratio. Using a hydraulic press (Montequipo, México LAB-30-T) the cylindrical samples (diameter of 2 cm and thickness of 0.3 cm) were made by uniaxial pressing at 30 MPa. Compacted samples were then sintered at 1673, 1773 and 1873 K for 3 h in a high temperature electric furnace (Nabertherm, Germany LT 15/13). The sintering process was carried out in the presence of an argon protective atmosphere. After the sintering, physical characterization of the composites was carried out to determine their density according to the Archimedes' principle, fracture toughness was determined using the indentation fracture method employing the equation proposed by Evans.[16] The hardness was determined according to ASTM E384–16 standard.[17] Structure crystalline was determined by DRX (Siemens, Germany, D-5000). The microstructural characteristics of the composites was observed by SEM (Jeol, Japan 6300).

3. Results and Discussion

3.1. Particle Size Distribution

Fig. 1 shows the diffraction spectra of the mullite/Ag composites sintered at 1873 K for 3 h for different compositions under study. At 2θ of 39.65 and 78° peaks appear with different intensities, which indexation corresponds to the 111, 200 and 311 planes of the cubic structure of silver. The remaining peaks observed in the diffraction patterns correspond entirely to the orthorhombic crystal structure of mullite. In this figure it is evident that intensity of reflections decreases notably and peaks become broader after milling. This effect is related with microstructural changes due to plastic deformation such as crystallite size reduction and lattice strain rise, both induced by high-energy ball milling.

Determination of the crystallite size in the mechanically milled powders is important since the phase constitution and transformation characteristics appear to be critically dependent on it. Suryanarayana[18] mentions that the crystallite size effect is more important, meanwhile M. Mansoor[19] suggests that the increase in the lattice strains (which is commonly related to crystal defects) mainly contribute to the strengthening of samples.

The lattice constants calculated from the XRD data for mullite a = 7.553 Å, b = 7.676 Å, c = 2.886 Å, cell volume V = 167.3 Å, with orthorhombic structure agree with the reported XRD data.[20] On the other hand, the lattice constants calculated from the XRD data for silver are a = b = c = 4.0847 Å, cell volume V = 68.152 Å, with face center cubic structure.

The crystallite size for resulting composite was calculated using the Debye–Scherrer Eq. (1).[21]

$$D = \frac{0.9\lambda_{k\alpha}}{B_{2\theta}\cos\theta} \tag{1}$$

where D is the crystallite size, 0.9 is the shape factors for spherical particles, k is the radiation wavelength (1.5406 Å), $B_{2\theta}$ is the full width at half maximum, and θ is the Bragg diffraction angle for the crystalline plane. The calculated value for the mullite crystallite size is 150.1 nm and 78.3 nm for the silver one. The initial materials have large crystallite size compared with the obtained mullite/Ag composite suggesting that after the intense mixing the reduction of particle size takes place. This condition favors the phenomena of diffusion to achieve a greater densification of composites, likewise, should have a better distribution of silver particles in the ceramic matrix, which would help in improving the mechanical properties.

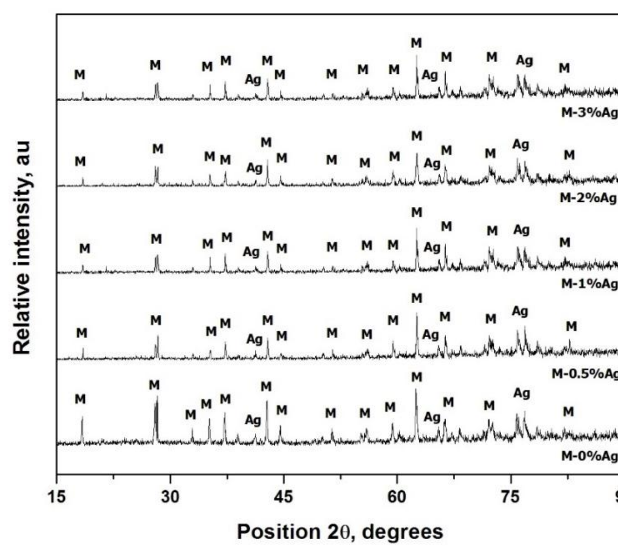

Fig. 1. XRD patterns of mullite composites with 0, 0.5, 1, 2 and 3 wt. % Ag sintered at 1873 K during 3 h

3.2. Density

Fig. 2 presents the results of the density measurements of mullite/Ag composites sintered during 3 h at different temperatures as a function of silver content. The density of the composites increases considerably by rising the sintering temperature. Likewise, densification of the samples is shown to be slightly higher with the increase in the silver content in the composite; however, in some cases values are very similar considering standard deviations. This behavior can be explained by the fact that silver, being a very good conductor of heat, favors the phenomena of diffusion in a significant way. On the other hand, at all sintering temperatures silver is in a liquid state (melting point 1235 K), which makes it necessary to study the sintering stage in the presence of a liquid phase. It has been reported in the literature that the good wettability of ceramics by silver is due to the low surface tension of the liquid,[22-23] this situation must considerably favor the mobility of atoms in the matrix, which stimulated densification of the composite.

With the respect to the effect of the sintering temperature on density, we observe the increase in density with the increase in the sintering temperature because the diffusion has a form of Arrhenius equation as it is shown in Eq. (1).

$$D = D_0\, e^{-a/RT} \qquad (2)$$

where D is the diffusion, D_0 is the diffusion coefficient of alumina, a is the activation energy, R is the universal gas constant and T is the temperature.

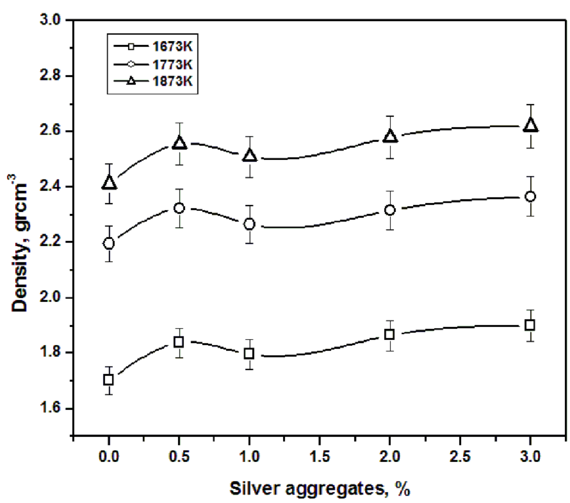

Fig. 2. Density of mullite/Ag composites sintered at 1673, 1773 and 1873 K during 3 h, as a function of silver content

3.3. Mechanical Testing

In the Figs. 3 and 4 the results of the microhardness testing using the Vickers scale and fracture toughness using the fracture toughness method are presented. After milling and sintering, the mechanical response of samples is increased and the mechanical properties can be measured. This behavior can be attributed to microstructural modifications, particularly crystallite size refinement[24] and lattice strain increase, where a larger fraction of grain boundaries means an enhanced mechanical behavior. This indicates that after intense mixing the mechanical response of samples increases and this condition is retained after sintering.

3.3.1. Microhardness

Fig. 3 shows the results of microhardness measurements on mullite/Ag composites sintered at different temperatures during 3 h as a function of the silver content. This figure shows the effect of a ductile metal such as silver on the mullite hardness (1070HV),[24] especially for the two sintered samples at the low temperatures (1673 and 1773 K). For the sample sintered at 1873 K, the microhardness of the composites is the closest to that reported in the literature for mullite.[24] In this case we observe a strong effect of temperature on the composites hardness, as well as the effect of adding even small amounts of silver. This increase of microhardness depends on both temperature and silver addition is and related to the better consolidation of the bodies as it was observed in Fig. 2.

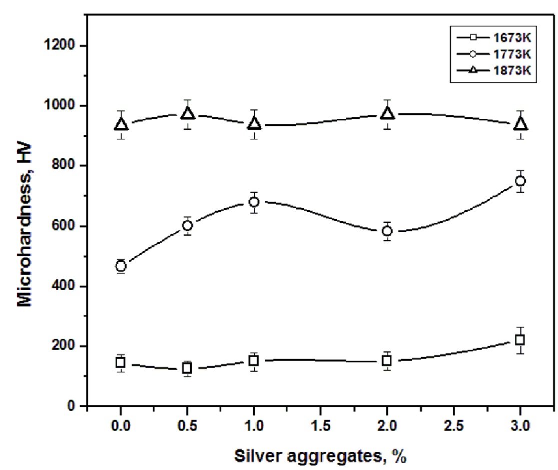

Fig. 3. Microhardness of mullite/Ag composites sintered at 1673, 1773 and 1873 K during 3 h for different concentrations of Ag

3.3.2. Fracture toughness

Fig. 4 presents the results of fracture toughness measurements on mullite/Ag composites sintered during 3 h at different temperatures as a function of the silver content in the composite. This figure shows the increase in fracture toughness for all silver additions and sintering temperatures. However, the effect shown by small silver content (0.5 wt. %) added to the mullite is insignificant to compare with silver content of above 1 wt. %, and especially with the maximum content of 3 wt. %. The silver addition, together with the increase in temperature, increases the fracture toughness of the composite from 2 $MPam^{0.5}$ (the value reported in the literature[29]) to 7 $MPam^{0.5}$, which represents a quite considerable increase of 350 %. This behavior proves that it is silver that has a significant effect on the mullite reinforcement. The latter statement is in accordance with the previously observed results, in which high operating temperatures together with high silver contents in the composites allow to obtain dense bodies with less porosity which favors the absence of sites (pores) for the initiation and propagation of cracks. Different authors have reported that the mechanism of ceramic reinforcement by metals occurs due to the crack bridging.[1] Obviously, a mechanism of this type must act in the reinforcement of the mullite by silver.

With respect to the effect of silver on the mechanical properties of the obtained composites, it is generally assumed that silver addition improves the hardness and fracture toughness, situations that are also favored by the increase in the composite density. In the case of hardness this effect is not so noticeable, because the standard deviations of the hardness values are within the same range for different silver contents. However, in the case of fracture toughness this effect is more obvious, especially when silver content is greater than 1 wt. %. During mechanical grinding, very small silver particles were obtained, which were evenly distributed in the ceramic matrix. Thus, as a crack grows through the ceramic matrix, it is very likely to collide with a metal particle in its advance, causing the crack to stop or deviate from its trajectory. Therefore, in order for the crack to continue to advance, it needs more energy, which leads to an increase in the strength of the ceramic. Due to this, the viscosity of mullite increases with increasing silver content.

As a summary, it can be seen that the composites with 3 wt. % of Ag have the highest hardness and fracture toughness. However, the results obtained show an improvement in these properties with increasing silver additions. So, according to the trend shown, the improvement in the properties could be expected for silver content above 3 wt. %. Therefore, this would be a good motivation for further work to investigate the effect of adding silver above 3 wt % on the mechanical properties of mullite.

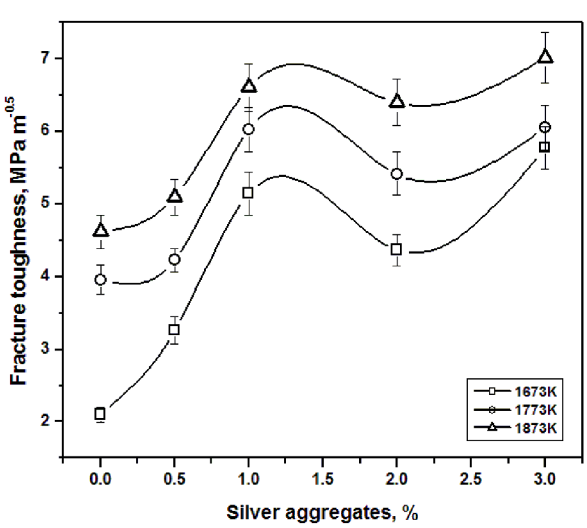

Fig. 4. Fracture toughness of mullite-Ag composites sintered at 1673, 1773 and 1873 K during 3 h for different concentrations of Ag

Fig. 5 represents a schematic diagram showing two possible mechanisms by which silver reinforces mullite. Fig. 5a shows the bridging of cracks due to the silver particles that prevent crack growth. As the crack advances, it encounters particles that cause it to deform before it can continue to advance further, leading to greater stresses and the crack can grow. Fig. 5b shows the crack deflection due to the silver particles that prevent crack growth. As the crack advances, it encounters the particles and must deviate its trajectory to continue to advance, which means more distance traveled and therefore more stress for the crack to grow.

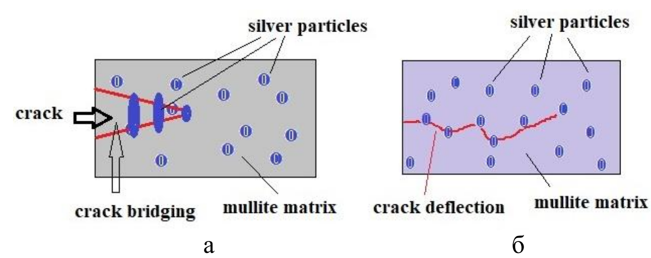

Fig. 5. Schematic representation of mullite reinforcement by addition of silver particles. (a) crack bridging, (b) crack deflection

3.4. Microstructure

As a general rule, the final microstructure after processing by mechanical milling, compaction and sintering strongly defines the mechanical properties of the prepared samples. Fig. 6 presents the microstructure of mullite/Ag composites sintered at 1873 K during 3 h. Fig. 6a, which corresponds to the sample without silver, shows a microstructure with disoriented grains in the form of filaments with sizes of approximately 5 microns. With the silver additions, the morphology of the grains changes drastically, with flake-shaped grains and rounded edges (Figs. 6 b, c, d and e). The approximate grain size in samples with silver is close to one micron, especially at higher silver contents. Although, the location of silver is not clearly observed in these micrographs, its presence is verified by EDS analysis in the sample with 3 wt. % of silver. The resulting spectrum from the EDS analysis is also presented in Fig. 6. This figure shows the mullite-forming elements, such as Al, Si, and O, and the presence of Ag reinforcements. With silver additions, the microstructure is finer and more homogenous, which helps to explain the better response of these composites in the fracture toughness. Silver has a direct impact on the microstructural characteristics, as it affects the morphology and grain size, and thus the mechanical behavior of mullite/Ag composites.

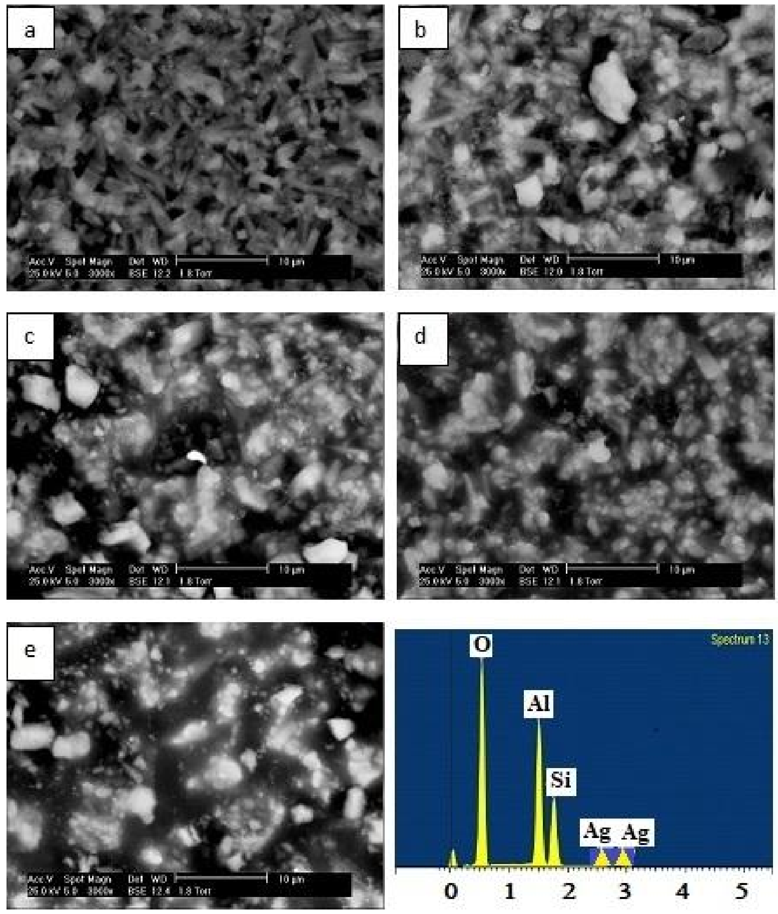

Fig. 6. SEM micrographs of mullite composites sintered at 1873 K for 3 h with 0 (a), 0.5 (b), 1 (c), 2 (d) and 3 (e) wt. % of Ag

4. Conclusions

− Through the proposed methodology, the mullite-based composites were obtained with improved fracture toughness due to the presence of a second dispersed phase of silver particles.

− In various evaluations of the properties of mullite/Ag composites, even the minimal presence of metal particles changes the behavior of the composites and leads to improved properties, increasing the density, hardness, and, most importantly, fracture toughness.

− The study shows that composites with 3 wt. % of Ag have the highest hardness and fracture toughness. However, the results show an improvement in these properties with an increase in the silver content. Hence, according to the trend shown, even an improvement in properties can be expected at a silver content of above 3 wt. %.

− The microstructure of the composites is strongly influenced by the presence of silver particles, as it changes from the presentation of grains as filaments randomly oriented for a sample without silver to grains as flakes for the samples to which silver has been added.

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Received: October 04, 2022 / Revised: January 28, 2023 / Accepted: July 04, 2023

ЗМІЦНЕННЯ МУЛІТОВОЇ КЕРАМІКИ АРМУВАННЯМ СРІБЛОМ

Анотація. *Композити на основі муліту, армовані частинками срібла, отримано порошковими методами. Спікання композитів проводили після інтенсивного змішування порошків прекурсорів. Виявлено, що добавки срібла мають значний вплив на механічні властивості, оскільки міцність на злам збільшилася до 350 %. Мікроструктура композитів представлена зернами з морфологією пластівців.*

Ключові слова: *муліт, керамічні композити, армування сріблом, міцність на злам.*