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Study on Corrosion and Thermal Alteration of MgAl_2O_4 and MgO Ceramics With Lead at 750°C for Use in High-Temperature Thermal Energy Storage

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ABSTRACT

Thermal-energy-storage (TES) systems are promising for decarbonizing industry by storing waste heat generated by high-temperature processes. Used as heat transfer fluid (HTF), liquid-metal-based TES offer a broad liquid operating range and high thermal conductivity, making them especially attractive. Directly combining a solid storage material with metallic heat-transfer fluid in a packed bed further increases stored energy while reducing the volume of liquid metal. Ceramics can be used as storage materials. However, liquid metals are highly corrosive. This study investigates the corrosion behavior of two grades of magnesium aluminate spinel (alumina-rich spinel, fused spinel) and three grades of magnesium oxide (94%, 97%, and 99% purity) exposed to static liquid lead at 750°C . The materials were analyzed using scanning electron microscopy and X-ray diffraction. The results show that all samples performed well overall. MgO showed better resistance than the tested spinels, with the highest-grade purity performing best. In all three grades, the magnesium oxide phase was stable; only the various calcium silicate phases observed at the grain boundaries reacted with Pb. Regarding the spinel, the fused one displayed cracks, and the alumina-rich one displayed Pb penetration and thermal alteration, resulting in a transformation of $\text{Mg}_{0.38}\text{Al}_{0.62}(\text{Al}_{1.79})\text{O}_4$, $\text{MgO}_{0.388}\text{Al}_{2.408}\text{O}_4$, and corundum Al_2O_3 , to $((\text{Mg}_4\text{Al}_{0.6})\text{Al}_{1.8}\text{O}_4)$.

1 | Introduction

High-temperature thermal energy storage (TES) is one possibility to increase waste heat recovery in the industry and provide heat on demand for other processes. Among those, TES systems capable of reaching temperatures above 650°C and having a high energy density are of particular interest for industries producing high-grade waste heat [1, 2]. A well-known example of TES is the system developed by Pacheco et al. [3] for a concentrated solar plant, which uses solar salts (60 wt.% NaNO_3 and 40 wt.% KNO_3) as heat-transfer fluid (HTF), with quartzite rocks and sand acting as filler material. However, solar salt is only stable up to 565°C because it decomposes at higher temperatures, releasing

toxic nitrous gases (NO_x) [4]. More recent publications indicate that nitrate salts can operate at temperatures up to 620°C if the oxygen and NO_x partial pressures are increased [5, 6]. Some studies even suggest that lithium chloride–lithium hydroxide salts (LiCl – LiOH)—can be used up to 700°C [7]. However, dissolved impurities in chloride salts can trigger rapid oxidation and metal dissolution, which can cause severe corrosion of the structural material at relevant temperatures [8].

In addition to molten salts, TES concepts using liquid metals (LMs) as HTFs are promising due to their high thermal conductivity 10–100 times higher than that of common liquids [9], and their wide liquid temperature range (for example,

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$T_{\text{Pb}} = 328\text{--}1749^\circ\text{C}$). These properties enable highly efficient charging and discharging processes in these TES systems, offering a compelling alternative to traditional HTFs. At the Karlsruhe Liquid Metal Laboratory (KALLA), a packed-bed sensible TES system has been successfully tested on a laboratory scale using lead–bismuth eutectic as a model HTF and ceramic beads (zirconium silicate) as the storage material [10]. The results demonstrated the general feasibility of such a system for the first time, and it was found that when using a storage material, the TES system performed better than when using a single-medium thermocline tank that utilized lead–bismuth only.

With regard to large-scale TES, lead (Pb) may be a suitable candidate as HTF, as it presents lower material cost while having similar heat transport properties to lead–bismuth [11]. At high temperatures (above 500°C), conventional structural materials may suffer corrosion from the contact with liquid metal, a liquid lead loop is currently being set into operation at KALLA to test components such as pumps and valves at temperatures of up to 700°C , serving as a basis to develop LM-based TES for elevated temperatures [12].

However, not only is the selection of compatible structural materials for tanks, pipes, components, etc. relevant, but also the testing of possible solid storage materials for high-temperature packed-bed TES. In the literature, ceramic materials have generally demonstrated good corrosion resistance to liquid metals like sodium, lithium, and lead at high temperatures [13, 14]. However, those studies lack depth in the explanation of the corrosion mechanisms and do not study the influence of the material's purity, which is a driving factor in storage material costs. The results from the lab-scale experiment developed at KALLA [10, 15] also prove a good compatibility of the studied alumina, steatite, zirconium silicate, and zirconium oxide with LBE at temperatures of up to 500°C .

Moreover, according to Guillon [16], ceramics in general “possess outstanding thermomechanical properties combined with high chemical stability, which makes them irreplaceable for high-temperature applications.” In the energy sector, they are used in various applications, such as nuclear power plants, concentrated solar power plants, and TES systems.

With regard to the application of ceramic material as a storage material in a TES, several works are reported in the literature, usually investigating them in combination with gases or molten salt as HTFs. Al-Azawii et al. [17] studied two types of ceramics for use as storage material in a sensible packed-bed TES with air as HTF: a recycled ceramic and alumina. The results of the study showed that at a temperature of 150°C , the alumina beads performed better than the recycled ceramic in terms of thermal exergy efficiency. Numerous further studies also mention the use of ceramics such as alumina, magnesia, or silicon carbide for use as storage materials in high-temperature ($T > 500^\circ\text{C}$) sensible TES systems [18–20]. Those studies demonstrated that ceramic material can compete with the currently used solar salt nitrates (NaNO_3 (60 wt.%)– KNO_3 (40 wt.%)), with the advantage of being stable over 600°C . Moreover, TES solutions for the industry using ceramics are already available on the market, such as the Eco-Stock solution developed by Eco-Tech Ceram using ceramics to store heat from 300 to 1000°C [21].

In addition to their use as solid storage material in TES, ceramics are also studied for use in latent heat storage as a coating or encapsulation material for phase change materials (PCMs). In this case, they are not used primarily for storing heat but rather as a structural material for containing the PCM, which stores heat through its phase change. The high thermal conductivity of ceramics makes them an excellent choice of material for PCM capsules, as stated by Fukahori et al. [22].

In summary, ceramics are excellent candidate materials for storing sensible thermal energy in packed bed TES and for encapsulation in latent TES systems. Moreover, they have already been shown to be generally compatible with metals. However, this compatibility has not yet been tested in detail, particularly for different grades of ceramic storage materials in contact with liquid lead (Pb).

Therefore, the purpose of this paper is to test five ceramic materials, two magnesium aluminate spinel (MAS) and three magnesium oxide ceramics, in contact with static molten Pb at 750°C . This temperature was chosen as a safety margin for a potential application of 700°C . This temperature is considered a significant improvement on the current state of storage materials for liquid metal-based TES (500°C [15]). In this publication, the materials are tested in static Pb only. If their corrosion resistance is demonstrated in this initial test, cyclic experiments will follow in a separate study. The exposure tests were preceded by a literature study of the thermophysical properties of the ceramics (density, heat capacity, and conductivity) to determine their suitability for a packed bed from the point of view of thermal capacity and heat transfer.

2 | Material Description and Physical Properties

The five selected ceramic materials were chosen for their high alumina and magnesia contents and are illustrated in Figure 1. The figure shows the different materials with increasing MgO content from left to right, namely, alumina-rich magnesium aluminate spinel (Al-rich MAS), fused MAS, natural dead-burned magnesium (DBM) oxide (MgO-1), magnesium oxide brick (MgO-2), and synthetic dead-burned magnesium oxide (MgO-3).

2.1 | Chemical Composition

The chemical composition of all materials was conducted at the Institute for Applied Materials – Applied Materials Physics (IAM-AWP), KIT. The chemical composition was determined by carrier gas hot extraction for element O and X-ray fluorescence analysis for the rest of the elements. The results for each material are listed in Table 1.

The alumina-rich magnesium aluminate spinel (Al-rich MAS) was supplied by Almatix GmbH under the name AR90. According to the data sheet, the material contains a minimum of 87 wt.% Al_2O_3 and 8 wt.% MgO [23]. The product was supplied in grade 3–6 mm. This type of spinel is typically used for casting in steel ladles, where the addition of spinel to aluminous refractory bodies improves their resistance to slag attack and thermal shock [23]. This type of spinel is manufactured in several stages. First, the

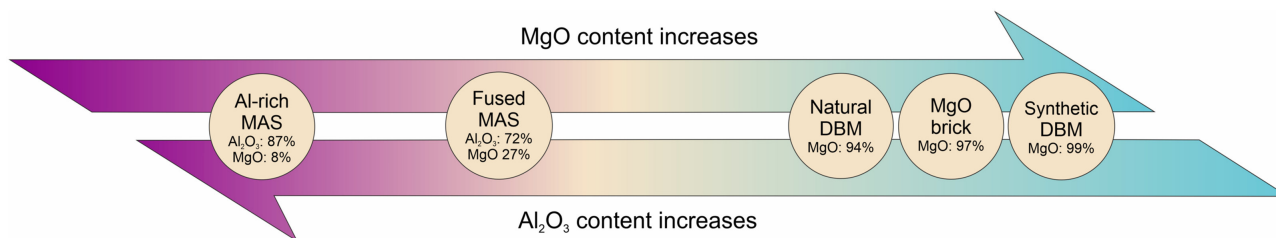


FIGURE 1 | Schematic compositional map of the selected materials, showing their Al_2O_3 and MgO content according to the respective suppliers (MAS, magnesium aluminate spinel).

TABLE 1 | Elemental composition (wt.%) of the studied material determined by carrier gas hot extraction (only element O) and X-ray fluorescence analysis (rest of the elements).

Material	O	Na	Mg	Al	Si	Ca	Fe
Al-rich MgAl_2O_4	45.5	0.057	6.20	47.4	0.12	0.11	0.10
Fused MgAl_2O_4	43.9	—	16.8	38.2	—	0.16	0.1
MgO-1	37.7	—	56.8	—	0.54	3.69	0.20
MgO-2	35.2	—	60.2	0.10	0.40	0.95	0.20
MgO-3	35.9	—	60.7	—	0.12	0.57	0.20

required oxides are calcined at temperatures above 1000°C . Then, the resulting magnesium aluminate spinel powder is densified and sintered at temperatures above 1900°C [24, 25]. X-ray fluorescence analysis of the sample showed a high purity consisting of 47.4 wt.% aluminum (Al) and 6.20 wt.% magnesium (Mg), with traces of calcium (Ca), silicon (Si), sodium (Na), and iron (Fe), as shown in Table 1.

A similar high purity but without traces of Si and Na was shown by the fused MAS, supplied by Imerys Fused Minerals Zschornowitz GmbH under the name TREIBACHER ALODUR MAS 2. The datasheet discloses a typical composition of 72.2 wt.% Al_2O_3 and a MgO content of 27.3 wt.% [26]. This spinel is manufactured by fusion in an electric arc furnace. Ganesh [24] describes this process, explaining that fused MgAl_2O_4 is obtained in a single step via the electrofusion of alumina and magnesia in an electric arc furnace at 2000°C . Similar to Al-rich MgAl_2O_4 , the fused MgAl_2O_4 can be used in refractories, ensuring a high resistance to abrasion and corrosive media due to its hardness and corrosion resistance.

Concerning the magnesium oxide used, the natural DBM oxide (MgO-1) was supplied from Lehmann&Voss&Co. KG. The lowest purity grade selected for this study, commercialized under the name W94, is of natural origin and is produced from magnesium carbonate. The resulting magnesium oxide is then calcined at a temperature above 1200°C . The maximal purity indicated

on the datasheet is 95.5 wt.% MgO on an ignited basis [27]. Mg and Ca exhibit similar chemical behavior, which makes it difficult to separate them completely during sample fabrication processing. Consequently, calcium is the predominant impurity in the sample, with a concentration of 3.69 wt.%. Additionally, trace amounts of Si and Fe were detected (see Table 1).

The second magnesium oxide in order of purity (see Table 1, MgO-2) was provided by the group of Coventry et al. from the Australian National University, currently developing a TES using liquid sodium as HTF [28]. The material was originally supplied by Zibo Hitech Material Co. with an indicated purity of 97–98 wt.% MgO [29]. Table 1 shows the results of the X-ray fluorescence analysis, which revealed traces of Al, Si, Ca, and Fe as impurities. This brick is typically used as a refractory brick in various applications.

The MgO with the highest purity grade (MgO-3) is also supplied by Lehmann&Voss&Co. KG and commercialized under the name M99. It is a DBM synthetic magnesium oxide produced from magnesium hydroxide, which is then calcinated at a temperature above 1200°C to remove moisture from the magnesium oxide. The supplier indicates a purity of 98.7 wt.% MgO on an ignited basis [27]. The measurements carried out showed additional impurities consisting of Si, Ca, and Fe (Table 1).

2.2 | Thermophysical Properties

Besides the corrosion behavior, the thermophysical properties such as density, thermal conductivity, specific heat, and volumetric heat capacity are crucial in selecting a suitable heat storage material. Therefore, this will be discussed in more detail later. An overview of the important thermophysical parameters for pure MgAl_2O_4 and MgO is given in Table 2.

The thermal properties of pure MgAl_2O_4 were taken from the literature and are assumed to be applicable for both selected MgAl_2O_4 , even though the values for the Al-rich MgAl_2O_4 might be slightly underestimated for the specific heat capacity and the density

TABLE 2 | Overview of the density, specific heat capacity, volumetric heat capacity ($\rho \cdot c_p$), and thermal conductivity of MgAl_2O_4 and magnesium oxide at 700°C .

Material	Density, $\text{kg} \cdot \text{m}^{-3}$	Specific heat capacity, $\text{J kg}^{-1} \text{K}^{-1}$	Volumetric heat capacity, $\text{MJ m}^{-3} \text{K}^{-1}$	Thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$	Source
MAS	3580 ^a	1334	4.7	7.7 ^b	[24, 30, 31]
MgO	3555	1266	4.5	8.6	[28, 32]

^aNo specific temperature is given in literature.

^bMeasured at 800°C .

and overestimated for the thermal conductivity [31, 33, 34]. Regarding thermal conductivity, Wu et al. [31] show that a higher Al_2O_3 content in the spinel leads to a reduction of the thermal conductivity. The measured conductivity at 800°C went from $7.7\text{ W m}^{-1}\text{ K}^{-1}$ for a stoichiometric MAS ($\text{Al}_2\text{O}_3\text{:MgO}$ ratio 1:1) to $5.9\text{ W m}^{-1}\text{ K}^{-1}$ for a $\text{Al}_2\text{O}_3\text{:MgO}$ ratio of 2.77:1. This change needs to be considered when designing a Pb-based TES, and the conductivity, heat capacity, and density of the selected material need to be carefully measured. The density was given by Ganesh [24]; however, no temperature was specified for this value. The specific heat capacity in $\text{J mol}^{-1}\text{ K}^{-1}$, $c_{p,\text{mol,MAS}}$, was calculated with the equation of Richet and Fiquet [30] (Equation (1)), which is validated until 1800 K. The conversion to $\text{J kg}^{-1}\text{ K}^{-1}$ is given in Equation (2). The thermal conductivity of the MAS is given by Wu et al. [31] at 800°C for pure MgAl_2O_4 .

$$c_{p,\text{mol,MAS}}/(\text{J mol}^{-1}\text{ K}^{-1}) = 242 - 8 \cdot \ln(T/\text{K}) - 3.87 \cdot 10^4 \cdot (T/\text{K})^{-1} + 2.2 \cdot 10^6 \cdot (T/\text{K})^{-2} - 4.26 \cdot 10^7 \cdot (T/\text{K})^{-3} \quad (1)$$

$$c_{p,\text{MAS}}/(\text{J kg}^{-1}\text{ K}^{-1}) = \frac{c_{p,\text{mol,MAS}}}{M_{\text{MAS}}/(\text{kg mol}^{-1})} = \frac{c_{p,\text{mol,MAS}}}{0.1421/(\text{kg mol}^{-1})} \quad (2)$$

The properties of pure magnesium oxide were calculated according to Bozorg et al. [28] and Chawla et al. [32] (see Equations (3)–(5)) with T representing the temperature in K. $c_{p,\text{MgO}}$ is the specific heat capacity (Equation (3)) and ρ_{MgO} the density (Equation (4)); both equations are valid up to 3000 K. λ_{MgO} is the thermal conductivity (Equation (5)), and the equation is valid up to 2200 K. In Equation (5), the coefficients were rounded to two significant digits for better readability here; for the original equation, please refer to [28].

$$c_{p,\text{MgO}}/(\text{J kg}^{-1}\text{ K}^{-1}) = 275.07 + 3.35 \cdot (T/\text{K}) - 4.8445 \cdot 10^{-3} \cdot (T/\text{K})^2 + 3.7854 \cdot 10^{-6} \cdot (T/\text{K})^3 - 1.6246 \cdot 10^{-9} \cdot (T/\text{K})^4 + 3.6106 \cdot 10^{-13} \cdot (T/\text{K})^5 - 3.2416 \cdot 10^{-17} \cdot (T/\text{K})^6 \quad (3)$$

$$\rho_{\text{MAS}}/(\text{kg m}^{-3}) = 3.65 \cdot 10^3 \cdot \exp(-3 \cdot 10^{-6} \cdot (-3.7483 \cdot 10^3 + 12.5491 \cdot (T/\text{K}) - 1.3512 \cdot 10^{-5} \cdot (T/\text{K})^2 + 3.0399 \cdot 10^{-7} \cdot (T/\text{K})^3)) \quad (4)$$

$$\lambda_{\text{MgO}}/(\text{W m}^{-1}\text{ K}^{-1}) = -2.16 \cdot 10^{-8} \cdot (T/\text{K})^3 + 7.52 \cdot 10^{-5} \cdot (T/\text{K})^2 - 0.09 \cdot (T/\text{K}) + 49.40 \quad (5)$$

Despite all three studied magnesium oxides not being pure substances, the calculated properties at 700°C are used here for the sake of a first evaluation of their general suitability with regard to their thermophysical properties.

Both ceramic material groups have a high volumetric heat capacity, being $4.7\text{ MJ m}^3\text{ K}^{-1}$ for MgAl_2O_4 and $4.5\text{ MJ m}^3\text{ K}^{-1}$ for MgO . This means that the materials can store an amount of

energy that is superior to that of ZrSiO_4 ($3.2\text{ MJ m}^3\text{ K}^{-1}$ [15]) used in the previous lab-scale experiment [10]. In comparison to solar salt ($\text{NaNO}_3\text{--KNO}_3$ (60–40 wt. %))—the state-of-the-art HTF and storage material used in CSP plants—with $2.7\text{ MJ m}^3\text{ K}^{-1}$ [35], almost double the amount of energy can be stored per volume compared with both investigated ceramic material groups in this study. Regarding thermal conductivity, no general conclusion can be drawn, as this depends on the application. When used for sensible TES, a low conductivity may be advantageous in reducing the growth of the thermocline region between hot and cold phases during standby periods, as the effective axial conductivity is the main driver for thermocline expansion [36]. However, another possible application is to use the ceramics as an encapsulation material in a latent TES. In this case, the thermal conductivity should not be sufficiently high in order to minimize thermal resistance. This application is, however, not the main focus of this study.

In conclusion, both the MAS and the MgO materials are evaluated as suitable candidates for use in a high-temperature packed-bed TES with Pb as HTF with regard to their thermophysical properties.

3 | Methods

3.1 | Experimental Set-Up

The static corrosion test in liquid lead was conducted at the COSTA (Corrosion Test Stand for Stagnant Liquid Alloys) facility at KIT-IHM [37]. The protocol used allows setting conditions that mirror the ones expected in a TES and which are identical to those detailed in previous work [38]. Static corrosion exposure tests were then carried out in a reducing atmosphere at 750°C . As lead has a higher density than that of the sample materials, the latter tend to float on the lead's surface. To ensure that the samples remain fully immersed in the liquid lead, they were mounted on an alumina holder using a molybdenum wire. The samples, which were initially at room temperature, were then immersed directly in an alumina crucible filled with molten Pb, which had been preconditioned at 750°C for several days.

A gas mixture of 95% argon and 5% hydrogen ($\text{Ar}5\%\text{H}_2$) was used in the furnace to create a reducing atmosphere during conditioning. Lead bars with a purity of 99.99%, supplied by Feinhütte Halsbrücke GmbH, were melted and poured into alumina crucibles. These were placed in a nickel tray to enable testing of multiple samples in parallel before being inserted into the quartz glass chamber. The COSTA furnace was then heated to a target temperature of 750°C . After that, the chamber was conditioned with a gas flow of 100 mL/min $\text{Ar}5\%\text{H}_2$.

The exposure duration was 1008 h. After exposure, the specimens were retrieved and prepared for corrosion behavior assessment.

The weight of the samples was not assessed before or after the experiment since a change in weight could be caused by several factors. As dissolution causes mass loss and lead infiltration causes mass gain, it would not have been possible to distinguish between these factors. The corrosion rate could hence not be assessed in this study.

3.2 | Preparation of the Samples

Regarding sample preparation, at least two samples from the same product batch were prepared and analyzed for each material. One sample was used as a reference and designated as the “original sample,” while another sample was taken from the exposure test and is referred to as the “exposed sample.”

Both the original and exposed samples were then prepared for microscopic analysis using the same method. The aim was to identify the microstructural phases of the material before and after exposure and to examine the interaction between the specimen and liquid lead. Both the surface and the cross-section of the samples were analyzed. For the cross-section preparation, the samples were embedded in resin, ground with SiC paper up to 2400-grit, and polished with a diamond suspension down to 1 μm . Finally, the samples were sputtered with gold to improve their electrical conductivity for scanning electron microscopy analysis. The exact protocol is described in detail in a previous paper [38]. For surface preparation, each sample was cleaned in a 1:1:1 mixture of acetic acid (CH_3COOH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and hydrogen peroxide (H_2O_2) to dissolve any lead agglomerate on the surface.

3.3 | Characterization of the Samples

All samples were analyzed and studied in terms of several factors: visual micro- and macroaspects and changes in chemical and crystalline structure.

After extraction from liquid Pb after 1008 h of exposure, each sample was inspected visually to identify any color change, fracture, or lead deposits. After this first inspection, a microscopic cross-sectional analysis was conducted using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS; Zeiss Leo 1530). This analysis was performed to evaluate the material interaction with Pb, including pore size distribution, penetration depth, cross-sectional morphology, elemental composition, and phase distribution. In addition, surface analysis was performed to investigate topology and any superficial reaction of the sample with Pb, which may explain the observed color changes.

The pore size distribution was analyzed using high-magnification SEM images, which were processed with software ImageJ. The area of each pore was calculated, and its equivalent diameter was subsequently derived.

X-ray diffraction (XRD) analysis was conducted on both the original and exposed samples to identify the crystalline structures before and after exposure. To perform XRD, the plane face of the cross-section was used. It should be noted that XRD analysis requires either a powdered specimen or a flat, polished surface. Therefore, separate specimens were used for the XRD analyses to avoid polishing the samples prior to exposure, which would have compromised their integrity and altered their initial surface condition. Only the original sample of the fused spinel was investigated in powdered form due to the low crystallinity of the sample. The XRD measurements were performed using Cu-K α radiation. SEM observations were used to support the interpretation of the results.

4 | Results

4.1 | Alumina-Rich Magnesium Aluminate Spinel

Figure 2a,b show a macroscopic and microscopic overview of the original sample. Figure 2c and d show the exposed sample. Figure 3a shows the XRD of both the original and exposed samples, and Figure 3b shows the pore size distribution for the studied specimen. Some additional pictures of the exposed sample are displayed in Figures 4a-d. The results regarding the original and exposed samples will be presented by comparing all of the mentioned recordings. The cross-sectional SEM image (Figure 2a) indicates a dense microstructure with a measured pore fraction of 7%. The associated EDS elemental distribution mapping, supported by point measurement results, reveals two different main phases: an Al-rich (Mg, Al) oxide and an Al oxide. In Figure 2b, an example of the composition of those two phases is given. The Al-rich (Mg, Al) oxide (around Point 1) had a composition of 9 at.% Mg, 28–29 at.% Al, and O. The Al oxide (around Point 2) had the following composition: 35–38 at.% Al and O.

As can be seen in Figure 3b, the pore size distribution is dominated by micropores measuring less than 5 μm . By contrast, pores larger than 20 μm are almost entirely absent, with the largest detected pore measuring approximately 40 μm . Fewer than 20% of the pores have diameters greater than 5 μm , indicating a microstructure characterized predominantly by fine pores. These pores are not connected, so they do not pose an acute threat to the material with regard to Pb infiltration.

Based on the XRD measurement results (see Figure 3a), the identified Al-rich (Mg, Al) oxide can be divided into two different (Mg, Al)O phases depending on the Al content: the higher-intensity peaks correspond to a nonstoichiometric Al-rich MAS, $(\text{Mg}_{0.388}\text{Al}_{2.408})\text{O}_4$ and $\text{Mg}_{0.38}\text{Al}_{0.62}(\text{Al}_{1.79})\text{O}_4$, whereas lower-intensity peaks are associated with stoichiometric MgAl_2O_4 . Second, the Al-rich oxide was identified as corundum. The phases observed are in good agreement with observations of Wu et al. [31], who investigated the influence of alumina content on various spinels and determined the phases present as a function of the Al_2O_3 content. Wu et al. [31] also reported that corundum forms with Al_2O_3 contents of around 90%, whereas only spinel is observed at 87.5% or lower. Given that the present sample contains a minimum of 87% Al_2O_3 , as seen in the datasheet of the product, the presence of corundum was expected.

After exposure, the previously white sample has changed to a gray color, as shown in Figure 2c. Significant changes in phase composition are also observed. XRD results reveal thermal alterations in the crystal structure of the sample, including a shift of the previously identified nonstoichiometric Al-rich spinel peaks to higher angles (see Figure 3a). In addition, the disappearance of corundum peaks indicates that its content has decreased below the detection limit of XRD. Consistent with these findings, EDS elemental mapping (Figure 2d) shows that the Al-rich phase, or corundum, is no longer present, and mostly only Al-rich (Al, Mg) spinel is observed. Point measurement (Point 3, Figure 2d) shows a composition of 6 at.% Mg, 32 at.% Al, and O. However, Al oxide is still locally present in very minor quantities in certain regions

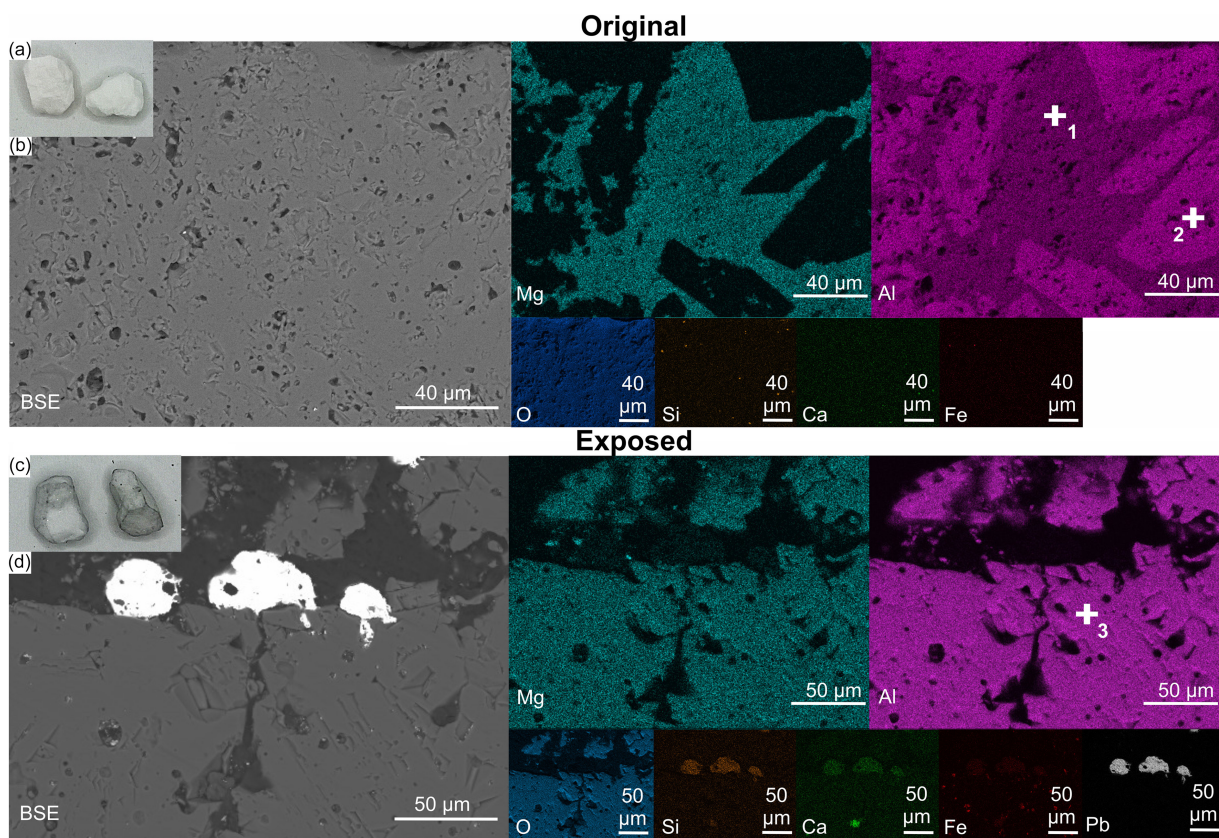


FIGURE 2 | Al-rich MAS samples. (a) Photograph of the original sample and (b) cross-sectional BSE image of the original sample with corresponding EDS elemental mapping. (c) Photograph of the exposed sample and (d) cross-sectional image of the exposed sample with corresponding EDS elemental mapping.

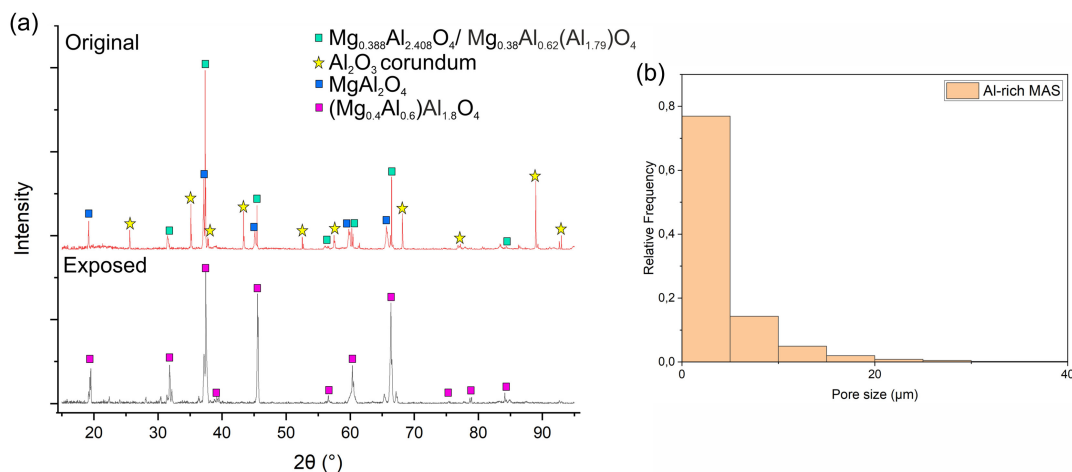


FIGURE 3 | Al-rich MAS. (a) XRD pattern of the original and exposed samples. (b) Porosity distribution diagram of the original sample.

measured. This behavior is attributed to the incorporation of Al into the spinel lattice at 750 °C, as evidenced by the 10–14% increase of Al content measured with EDS in the spinel phase compared to the original sample, leading to the transformation to $(Mg_{0.4}Al_{0.6})Al_{1.8}O_4$, a nonstoichiometric spinel phase. This is consistent with the observations reported by Wu et al. [24], explaining that several spinel phases can be formed with the general formula $Mg_{(1-x)}Al_{(2+2/3x)}\square_{1/3x}O_4$ and that the appearance of a specific spinel phase depends on the availability of magnesium and aluminum oxides during formation.

As mentioned, a slight darkening of the sample was observed macroscopically. This change is due to reaction of Pb with the sample's surface, which is highlighted in Figure 4a,c,d. The Pb-containing surface appears bright in the SEM image.

In the cross-section, cracks are observed running more than 2 mm into the bulk for a width of 6.4 μm (Figure 4b). These are most likely caused by thermal shock during sample loading or extraction from the liquid metal ($\Delta T \approx 725$ °C). Additionally, Pb penetration is visible inside surface defects, such as pores and

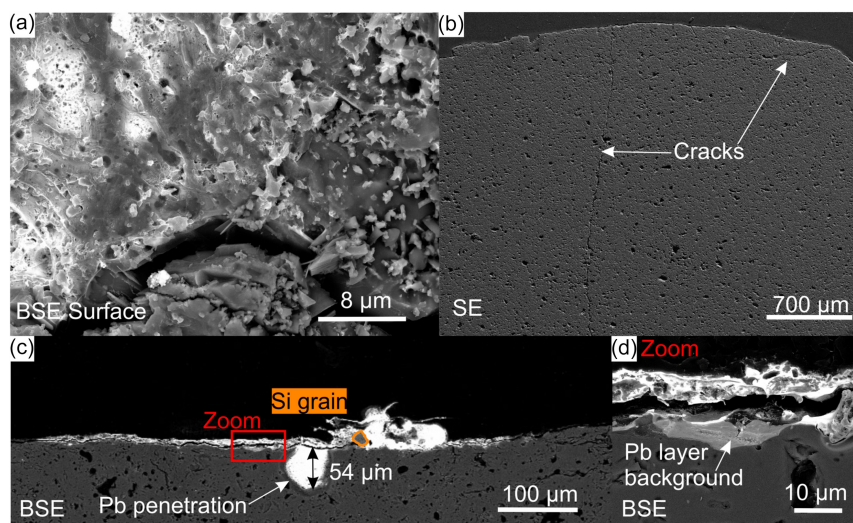


FIGURE 4 | Al-rich MAS after exposure. (a) BSE surface image with Pb penetration into pores, (b) SE image of the cross-section showing deep cracks, (c) BSE image of the cross-section showing Pb penetration, and (d) associated zoom showing Pb reaction on the edge of the sample.

indentations (Figure 4a,c). Moreover, a slight enrichment of Mg and Al could be detected in the Pb phase, most probably due to a slight solution attack (Figure 4c,d).

Figure 4d indeed shows a slight reaction between Pb, Al, Mg, and O, forming a thin surface layer ($\sim 1\ \mu\text{m}$), with an approximate composition of 2 at.% Pb, 24 at.% Al, and 3 at.% Mg and O. The amount of this phase is too low to be detected by XRD. It is also possible that a lead–aluminum–oxide complex compound forms, as already observed in literature. Heinzel et al. [39] described a $\text{Pb}(\text{Al}_2\text{O}_4)$ formation at 550°C in liquid Pb after 144 h exposure of a pulsed laser deposition coating consisting mainly of amorphous Al_2O_3 with few randomly distributed nanocrystalline $\alpha\text{-Al}_2\text{O}_3$. After longer exposure times (2000 and 3100 h) of preoxidized alumina containing ODS (oxide dispersion strengthened) samples at 600°C exposed to LBE, Li et al. [40] observed as well Pb–Al–O complex compounds.

Regarding the suitability of the material for use in packed-bed TES, it is to be noted that the thermal properties may vary depending on the $\text{Al}_2\text{O}_3\text{:MgO}$ ratio. According to the presented results and the analyses of Wu et al. [31], the molar $\text{Al}_2\text{O}_3\text{:MgO}$ ratio in this work is assumed to range from 2.77:1 to 3.56:1. This provides insight into the thermal properties of the sample (see Section 2.2), which are suitable for use as a TES storage material. Furthermore, as Pb penetration was only observed in a limited area of the cross-section, it can be considered negligible.

In summary, the material behaved well in stagnant Pb and would be suitable for use in a TES.

4.2 | Fused Magnesium Aluminate Spinel

The following supports will be used for the fused MAS analysis. Figures 5a and 5b show macroscopic and microscopic overviews of the original sample, respectively. Figures 5c and 5d show the exposed sample in a similar way. Figure 6a–d provides additional information regarding the behaviour of the sample with Pb. Figure 7a shows the XRD of both the original and exposed samples

and Figure 7b shows the pore size distribution. The findings concerning the initial and exposed specimens will be displayed by juxtaposing all the mentioned images. The original fused MAS sample is white in color, almost translucent, and exhibits a dense microstructure with a measured porosity of 8% (Figure 5a,b). Some cracks are also observed (see Figure 6a). Figure 5b shows the microstructure of the sample as well as its associated elemental mapping, revealing the presence of two distinct phases. Based on EDS point measurements, the dominant phase consists of 14 at.% Mg and 28 at.% Al, which is confirmed by XRD in Figure 7a as MgAl_2O_4 . A secondary needle-like phase showed an oxide formed with 2–3 at.% Na, 23–26 at.% Al, 1–5 at.% Si, 9–15 at.% Ca, and O. Due to its low abundance, this phase could not be identified by XRD and is therefore referred to as the Al–Ca–Na–Si–O phase. Both phases are also highlighted in Figure 5b where the Al–Ca–Na–Si–O phase appears brighter than the MgAl_2O_4 phase.

As observed in Figure 7b, this sample exhibits significantly larger pores than the other materials, with some reaching diameters of up to $280\ \mu\text{m}$. Although pores of this size account for less than 2% of the pore population, they may provide preferential pathways for lead (Pb) penetration.

A visual examination of the original and the exposed sample (Figure 5c) reveals a darkening of the sample's surface after exposure, caused by localized Pb surface reaction, similar to the Al-rich MgAl_2O_4 sample. Figure 6c,d shows such an area with an associated EDS line measurement, revealing a diffusion of Pb into the surface. Furthermore, needlelike crystals, which are attached to the surface, are formed (Figure 6c). Concerning EDS line scans, it seems to be a compound of Pb–Na–Al–Mg–O. A study by Tunca et al. [41] highlights the mechanism by which the solid solution $\text{Zr}_2(\text{Al}, \text{Bi}, \text{Pb})\text{C}$ forms after Zr_2AlC is exposed in liquid lead–bismuth eutectic under reduced oxygen conditions. The authors explain that Al, being the most soluble element of the system in LBE, could have undergone selective leaching when in contact with LBE. This mechanism could also be applicable to the present study. In the present attacked oxide compound, Al–Ca–Na–Si–O, several elements are soluble in Pb, ranked as follows: $s_{\text{Na}} > s_{\text{Mg}} > s_{\text{Ca}} > s_{\text{Al}}$. Na is the most soluble element, with

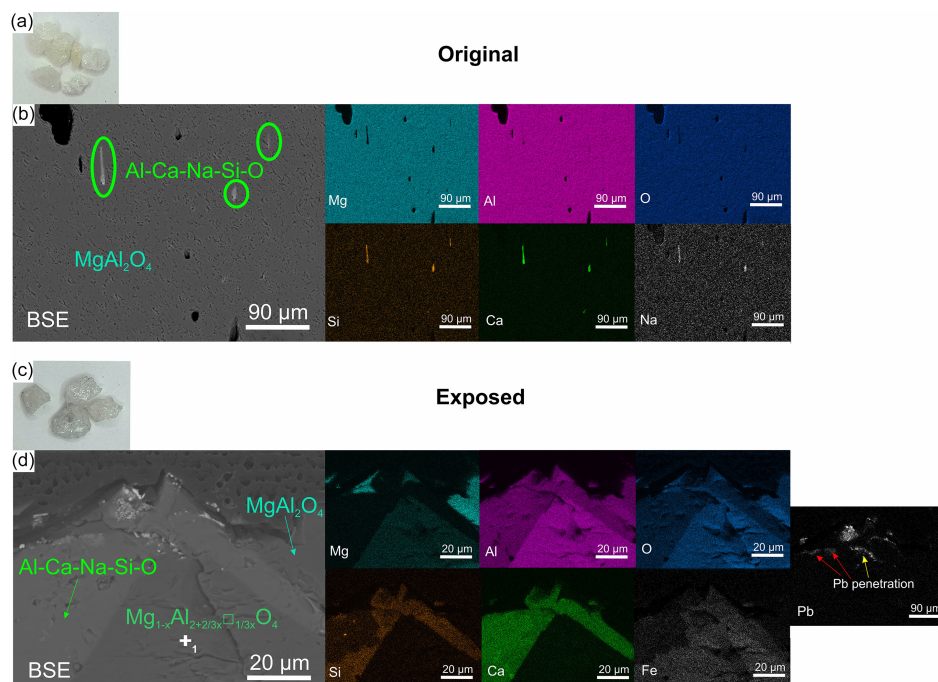


FIGURE 5 | Fused MAS. (a) Photograph of the original sample, (b) elemental mapping highlighting the different phases observed in the original sample, (c) photograph of the exposed sample, and (d) cross-sectional image with Pb reaction and associated EDS elemental mapping.

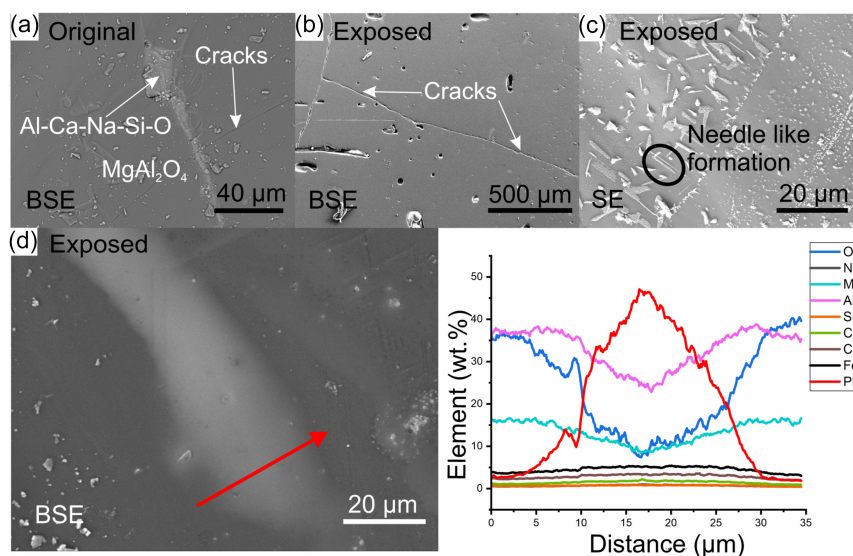


FIGURE 6 | Fused MAS. (a) Cross-sectional BSE image of the original sample showing cracks, (b) cross-sectional BSE image of the exposed sample, (c) needlelike deposit formation at the surface of the sample (SE image), and (d) surface with Pb reaction (bright area) and associated line measurement along red arrow.

a solubility close to 100 mol% in Pb at 600 °C, while Al has a solubility of around 0.13 mol% [42].

As the compound is an oxide, its corrosion resistance should be high; however, some Na or Mg may have diffused outward, and the phase may have experienced selective leaching of Na or Mg by Pb.

Cross-sectional analysis reveals a noticeable increase in crack number compared to the original sample (Figure 6b). These cracks may have resulted from the high thermal shock experienced by the sample when it was placed in the furnace; the glass phase in the sample favors this behavior. The sample also exhibits

the highest overall porosity (10%) among all the materials investigated, with some pores measuring to 280 μm, which may explain its comparatively poorer performance and crack appearance. In addition, Pb penetrates up to 30 μm into the bulk and reacts mainly with the secondary phase containing Si, Ca, and Al, as shown in Figure 5d (red arrows). Pb ingress along the cracks is also observed, as marked by the yellow arrow in Figure 5d.

No changes in phase composition are observed before and after exposure. Variations in peak intensities can be attributed to differences in the measurement method. Due to a poor result obtained on the cross-section, the original sample was analyzed as a fine

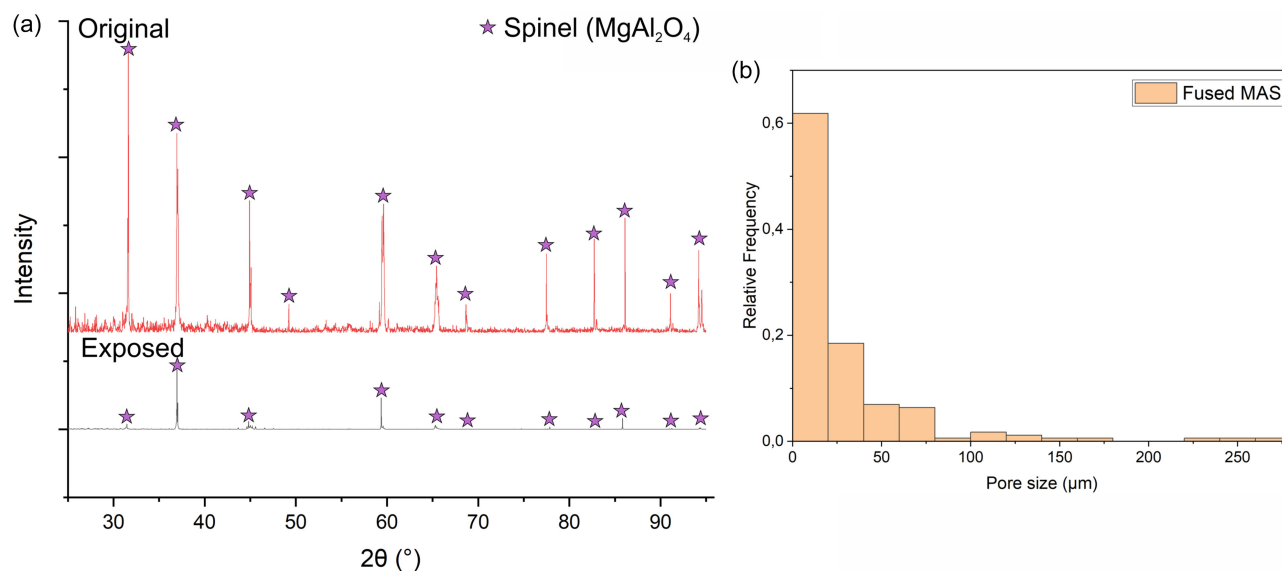


FIGURE 7 | Fused MAS. (a) XRD pattern of the original and exposed samples. (b) Porosity distribution diagram of the original sample.

powder, whereas the XRD measurement of the exposed sample was successfully performed on its cross-section. Therefore, the differences in peak intensities observed between the original and exposed samples are most likely due to the use of different specimens and sample geometries for the analyses rather than being caused by thermal alteration.

Overall, except for a few leaching areas, the interaction of Pb with the fused spinel is negligible. However, the material appears to exhibit low thermal shock resistance, resulting in an increased crack density. This needs further investigation. As discussed in Section 2.2, its thermophysical properties are suitable for a TES, and its chemical composition composed of stoichiometric MAS makes it easier to predict the future properties of the material compared to the previous MAS.

4.3 | MgO-1

Figures 8a,b and 8d,c provide an overview of the macroscopic and microscopic structure of the original and exposed MgO-1. The associated XRD is presented in Figure 9 and will serve as the basis for analysing the behaviour of MgO-1 in Pb. The microstructure of the original MgO-1 sample (Figure 8b) exhibits a typical polygonal grain morphology, consistent with that of MgO reported in the literature [34]. The average grain size was measured to be in the range of 60–70 μm. Due to the high density of cracks observed throughout the sample, a reliable quantification of porosity was not possible. EDS point analysis and elemental mapping revealed the presence of two distinct phases: a primary MgO phase and a secondary Ca–Si–O-based phase. Quantitative EDS analysis of the primary phase (Figure 8c, point 1) indicates a composition of 47–48 at.% Mg and O, which is consistent with MgO and in agreement with the XRD results (Figure 9). The intergranular phase along the grain boundaries of the MgO matrix acts as bonding between adjacent grains. EDS mapping, as shown in Figure 8c, reveals an enrichment of Si and Ca at this location. However, their distribution is not uniform. Two distinct intergranular phases can be identified: a Ca-rich Ca–Si–Mg–O phase and a Si-rich Si–Ca–Mg–O phase.

Macroscopic inspection reveals only a slight surface color change (Figure 8d), along with traces of attached Pb on the surface, as also observed in Figure 8f.

It has been observed that Pb penetration occurred primarily along the intergranular Ca–Si–Mg–O phases (Figure 8e (Pb)), which appear porous and thereby facilitate Pb penetration. The maximum depth of Pb penetration was determined to be approximately 46 μm. Surface analysis also confirmed that Pb is predominantly detected in the intergranular phases (Figure 8f), indicating that these regions act as the main pathways for infiltration. In contrast, MgO grains remain unaffected by Pb. These observations are consistent with the XRD analysis results shown in Figure 9, which show no detectable changes before and after exposure. The intergranular phases could not be detected in XRD due to their low abundance.

Overall, MgO-1 exhibits good behavior in general; however, the presence of large pores and cracks, combined with the interaction of Pb with the bonding intergranular phase, may promote material degradation during operation in heat storage systems. Moreover, even if the sample exhibits suitable properties for use as a storage material for a TES (Section 2.2), the sample seemed more brittle than the other studied ceramics, and its fracture strength should be investigated before being used in a TES. If the sample is too brittle, the material could be destroyed due to the weight of the packed bed or the thermal contraction induced during discharging.

4.4 | MgO-2

Figures 10a–c present macroscopic and microscopic overviews of the original MgO-2 sample, and Figures 10f–i for the exposed MgO-2 sample. Figure 11 shows the XRD patterns for the original and exposed samples, enabling a comparative analysis of structural changes. The MgO-2 brick sample exhibits a heterogeneous microstructure and a high porosity, which could not be measured due to a low overall densification. Locally, coarse-grained regions are observed, with grain sizes in the

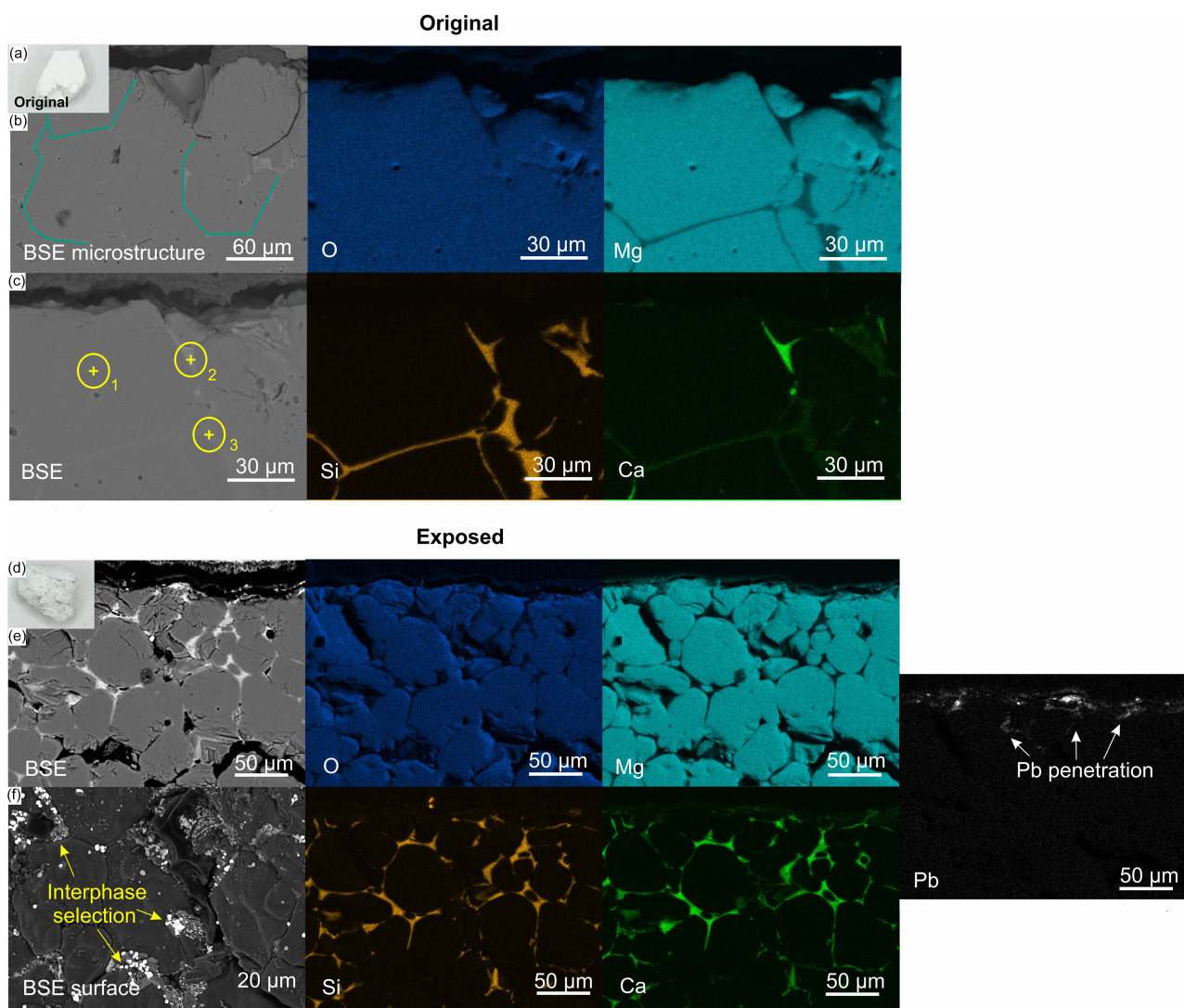


FIGURE 8 | MgO-1. (a) Photograph of the original sample, (b) cross-section of the original sample showing the microstructure (BSE image), (c) cross-section of the original sample, associated EDS mapping and point measurement location highlighted in yellow (BSE image), (d) Photograph of the sample after exposure, (e) cross-section of the exposed sample and associated EDS mapping, and (f) surface of the sample (BSE image).

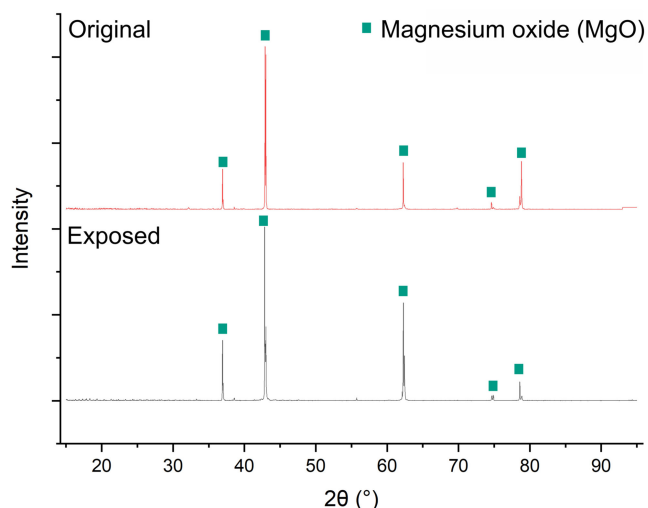


FIGURE 9 | MgO-1. XRD pattern of the original and exposed samples.

range of 200–300 μm (see Figure 10b,c). Representative images and corresponding elemental mapping (Figure 10b) show a microstructure composed of well-defined polygonal grains and two distinct phases. EDS point measurements and XRD analysis identify the primary phase as MgO (see XRD results in Figure 11). Compared to MgO-1, the sample exhibits a lower Ca content and contains trace amounts of Al (see Table 1). In contrast to the previously described MgO-1 sample, the element mapping of MgO-2 shows only one intergranular phase, being a Ca–Si–Mg oxide with traces of Al. Its composition is measured as follows: 16–20 at.% Ca, 11–13 at.% Si, and 7–15 at.% Mg and O.

The original sample is red in color (see Figure 10a). This red color is attributed to the presence of iron oxide. According to EDS mapping (see Figure 10b), iron oxide appears to be evenly distributed. After exposure, visual inspection of the sample revealed a significant change in color: the originally reddish MgO-rich matrix had become predominantly white with a few black spots visible (see Figure 10f). This change in color may result from a reducing atmosphere inducing chemical

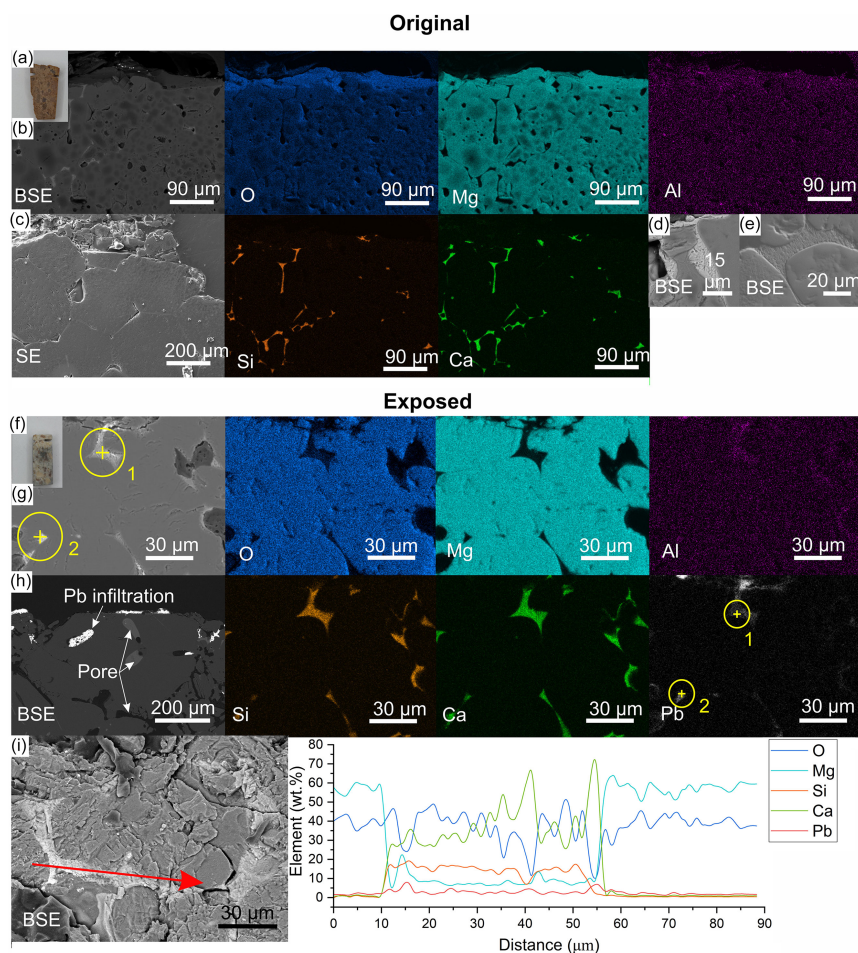


FIGURE 10 | MgO-2. (a) Photograph of the original sample, (b) cross-section of the original sample and associated mapping, (c) cross-section of the original sample showing the microstructure (SE image), (d) zoom on intergranular phase with porous microstructure (BSE image), (e) with laminar microstructure (SE image), (f) photograph of the exposed sample, (g) cross-section of the exposed sample with associated EDS elemental mapping, (h) cross-section (BSE image) of the exposed sample showing Pb penetration inside the pores, and (i) BSE image of the surface of the exposed sample and associated line measurement along the red arrow.

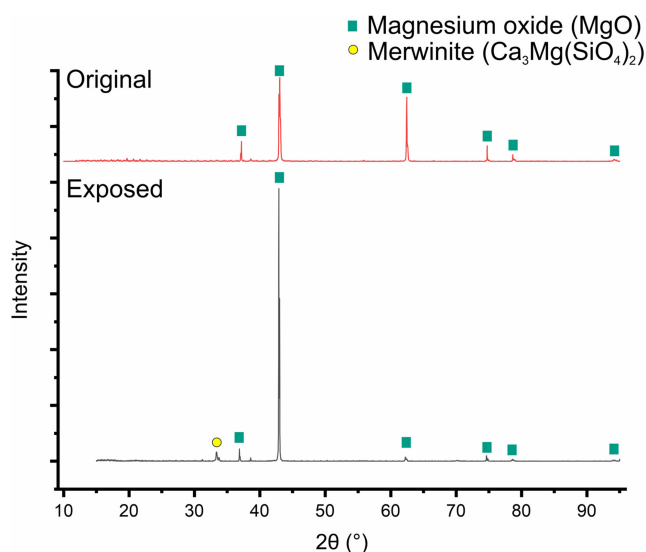


FIGURE 11 | MgO-2. XRD pattern of the original and exposed samples.

transformations from hematite to magnetite, as reported in the literature [43, 44]. Another possibility is that the Fe is incorporated into the Ca–Si–Mg oxide at high temperatures, as it is known to form clay during firing [45]. However, these theories could not be verified using SEM or XRD measurements, and point measurements at the surface of the sample did not reveal a significant change. Point measurements showed 0.11 at.% Fe at the surface of the original sample and 0.10 at.% Fe at the surface of the exposed sample.

Images of the MgO-2 sample surface after exposure reveal an intergranular phase reaction with Pb. Line measurement in Figure 10i shows that on the sample's surface, Pb is found with Mg, Si, and Ca, i.e., in the intergranular phase only. This is also visible in the cross-section in Figure 10g where EDS elemental mapping shows that Pb only occurs alongside Ca and Si up to a depth of around 80 μm. Point 1 shows 1–2 at.% Pb with 7–8 at.% Mg, 12–13 at.% Si, and 18–21 at.% Ca and O, and Point 2 shows up to 5 at.% Pb with Mg, Si, Ca, and O. The intergranular phases exhibit a noncompact or porous morphology, which likely facilitated the infiltration of Pb during exposure. The main MgO phase does not appear to have been attacked by the liquid metal. Additionally, large pores and cracks (see Figure 10h)

may provide further pathways for Pb to penetrate the bulk material, potentially leading to its destruction over time.

The XRD map of exposed and nonexposed sample surface can be seen in Figure 11. While the original sample exhibits only an MgO phase, the exposed sample shows additional peaks of merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$. This is due to change of measurement surface used; the original sample was analyzed on the sample surface, and the exposed sample was analyzed on its cross-section, presenting locally more intergranular phase, allowing for its detection by XRD.

In summary, Pb penetration is deeper in the MgO-2 sample than in the other materials, due to large pores and cracks, as well as its interaction with the intergranular phase. Thermal cycling and pressure tests are recommended for further evaluation. It should be noted that, due to the large MgO-2 grain size, the material will exhibit greater volume loss when subjected to degradation. However, even if the material seems to present the worst corrosion resistance compared to the other ceramics of this study, MgO-2 performed better than other studied materials in contact with Pb at 750 °C, like quartzite brick or steel slag, which all presented phase transformations, deep cracks, and Pb reaction [38].

Moreover, MgO-2 presents an advantage regarding its integration in a TES. If used in a rectangular tank, its brick shape allows for a dense packing, bringing the porosity up to 5% according to Bozorg et al. [28], which is an important reduction compared to the minimal porosity of 22%, given in the literature for a polydispersed bed [3, 46, 47]. When using MgO as a storage material, a reduction of the bed porosity allows for a reduction of the HTF used and thus a reduction of the cost [11]. While presenting suitable thermophysical properties (see Section 2.2), the use of MgO-2 for a TES must be carefully monitored due to the potential degradation mentioned above.

4.5 | MgO-3

Figure 12a-c and 12d-e respectively depict the original and exposed MgO-3 samples, with additional detailed observations of the exposed MgO-3 provided in Figure 13a-g. Figure 14a illustrates the XRD analysis for MgO-3, and Figure 14b highlights the pore size distribution. These visual aids are collectively compared offering a comprehensive understanding of the behavior the sample in its original and exposed state.

Similarly to MgO-2, MgO-3 has a reddish color (Figure 12a). The sample shows a denser and more homogeneous microstructure compared to other MgO samples (Figure 12b), with a lower porosity of 2–3% and a finer grain size of 30–50 μm. The chemical composition of the MgO-3 sample (see Table 1) indicates a higher Mg content and lower impurities such as Si and Ca compared to MgO-1 and MgO-2, reflecting its higher purity. The surface of the original sample, as shown in Figure 12c, shows the characteristic polygonal MgO grains separated by an intergranular phase. This intergranular phase has a chemical composition of 10–12 at.% Ca, 25–28 at.% Mg, and locally 4–6 at.% Si and O, as determined by EDS point measurements. Furthermore, the fraction of the intergranular phase is lower due to the higher purity of the sample.

As shown in Figure 14b, 46% of the pores measured have diameters between 0 and 2 μm, while 37% fall within the 2–4 μm range. The remaining pores are distributed up to a maximum size of approximately 10 μm. The pores are predominantly located along the boundaries between MgO grains. Overall, this sample exhibits the lowest porosity, with pores being predominantly smaller than 10 μm. The limited pore size is expected to reduce pore interconnectivity, thereby decreasing the likelihood of continuous pathways for Pb penetration.

After exposure to liquid Pb for 1008 h, no visible color change was observed on the sample (Figure 12d), unlike other MgO samples. However, an increased number of cracks at the sample edges is observed after exposure (see Figure 12e). Cross-sectional SEM image has shown that no significant Pb penetration into the bulk was observed. Pb is primarily found near the sample surface and locally within pores. This behavior is likely attributed to the relatively dense microstructure of the material and the low amount of the intergranular phase. To further investigate the corrosion behavior, the sample surface was examined after cleaning. After the cleaning process, the intergranular Ca–Mg–O-rich phases were found to dissolve in the cleaning solution. Whereas the intergranular residual phases associated with Pb remained and could be observed (see EDS elemental mapping in Figure 13). EDS point analysis of the regions revealed an oxide with approximately 6–11 at.% Ca, 19–25 at.% Mg, and 4–6 at.% Pb, suggesting the formation of Ca–Mg–Pb–O phase.

The XRD patterns in Figure 14a of both the original and exposed samples show no differences. No significant Pb penetration is observed, which is attributed to the dense microstructure and low amount of intergranular phase.

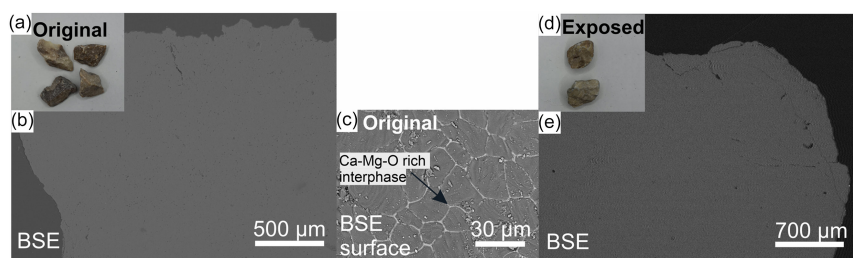


FIGURE 12 | MgO-3. (a) Photograph of the original sample, (b) low-magnification image of the cross-section of the original sample (BSE image), (c) surface of the original sample showing the microstructure (BSE image), (d) photograph of the exposed sample, and (e) low-magnification image of the cross-section of the exposed sample (BSE image).

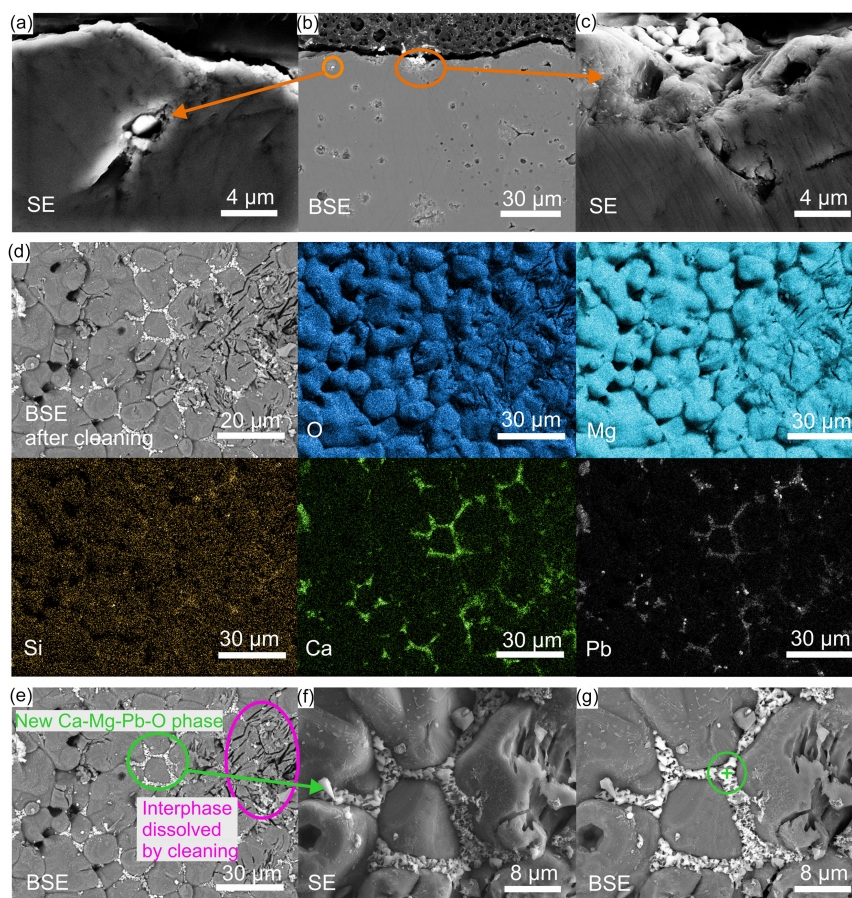


FIGURE 13 | MgO-3. (a) Zoom on Pb deposit (SE image), (b) overview of the cross-section of the exposed sample, (c) zoom on Pb deposit (SE image), (d) EDS mapping of the surface of the exposed sample after cleaning, (e) surface of the exposed sample after cleaning (BSE image), and (f), (g) zoom on the intergranular phase having reacted with Pb (SE and BSE image).

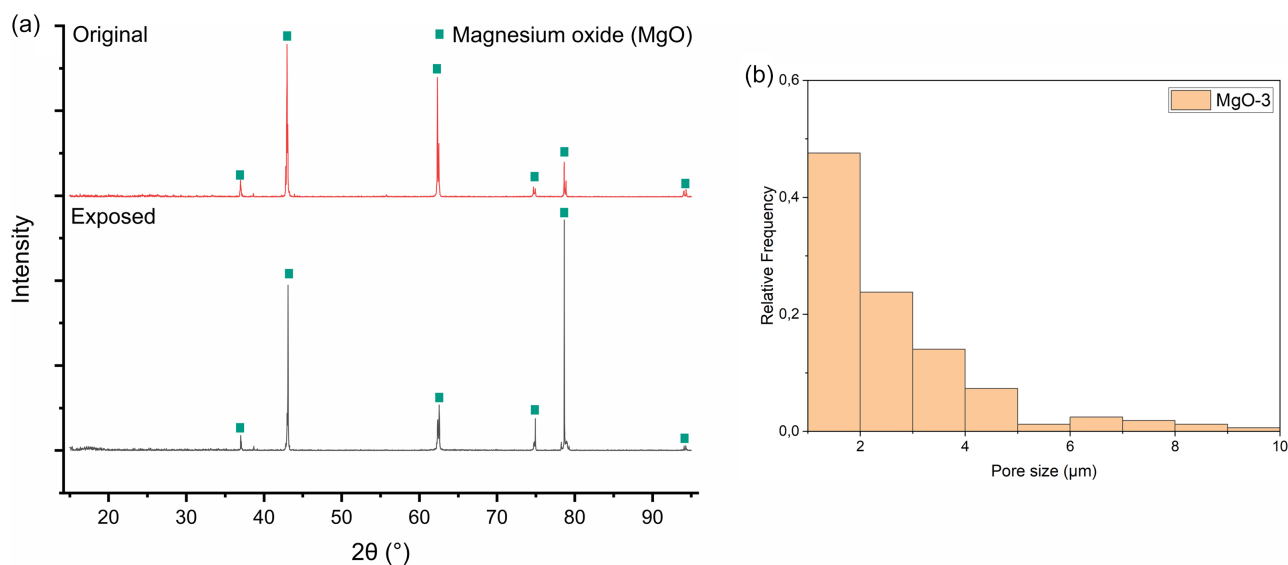


FIGURE 14 | MgO-3. (a) XRD pattern of the original and exposed samples. (b) Porosity distribution diagram of the original sample.

MgO-3 presents the best corrosion resistance among the materials investigated in this study. Its high-temperature stability and excellent corrosion resistance make it particularly suitable for demanding operational environments, which is Pb-based TES. However, due to the observed increase in crack density

on the edges, further testing is required. Regarding its properties, the high volumetric heat capacity of $4.5 \text{ MJ m}^{-3} \text{ K}^{-1}$, determined in Section 2.2, further enhances its performance potential. Compared to the currently used ZrSiO_4 [10, 15], this material demonstrates superior storage capacity, indicating an

TABLE 3 | Comparison of the studied materials and main observations relating to their behavior with Pb.

Material	Phase 1 (major phase)	Phase 2	Phase 3	Main observation	Corrosion resistance
Al-rich MgAl ₂ O ₄	Mg–Al spinel (58%)	Al ₂ O ₃ (42% min)	—	Cracks, formation of Pb–Al– Mg oxide	Good
Fused MgAl ₂ O ₄	MgAl ₂ O ₄ (98%)	Al–Ca–Na–Si–O intergranular phase (2%)	—	Cracks, up to 8 wt.% Pb in intergranular phase	Good
MgO-1	MgO (94%)	Ca-rich Ca–Si–Mg–O intergranular phase (4%)	Si-rich Si–Mg– Ca–O intergranular phase (2%)	Only 1 wt.% Pb in intergranular phase	Good
MgO-2	MgO (97%)	Ca–Si–Mg–O intergranular phase (3%)	—	Cracks, Up to 31 wt.% Pb in interregion (phase 2)	Fair
MgO-3	MgO (99%)	Ca–Mg–(Si)–O intergranular phase (1%)	—	Pb reaction with intergranular phase	Excellent

advancement in material applicability. Furthermore, according to previous study [11], MgO is a promising material to reduce material cost of storage. However, due to its nonspherical shape, stress may arise in the tank during cycling. To avoid thermal ratcheting, further studies need to be conducted.

5 | Conclusion

The chemical compatibility of five different ceramics with molten Pb was investigated to evaluate their feasibility as storage materials in a packed-bed TES system using Pb as HTF. Two grades of magnesium aluminate spinel and three grades of magnesium oxide were exposed to molten Pb at 750 °C for 1008 h under stagnant conditions.

- The Al-rich MAS sample exhibited deep cracks up to 2 mm. Ultra-thin near-surface formation of Pb–Al–Mg oxide was observed only locally. Additionally, interaction between Al₂O₃ and MgAl₂O₄ phase at 750 °C appears to lead to the formation of a nonstoichiometric Mg–Al–O spinel.
- The fused MAS sample exhibited a high number of cracks, probably induced by high porosity and low thermal shock resistance and near-surface Pb diffusion into the secondary Al–Ca–Na–Si–O phase. The main spinel phase remained stable.
- The highest purity MgO (MgO-3) showed the best behavior due to its dense structure and low fraction of intergranular phases. In all MgO materials, the intergranular phases consisting mostly of Si–Ca–Mg–O, show an affinity for Pb. In contrast, the MgO-2 brick sample exhibited the poorest performance due to its low densification and the presence of defects such as pores and cracks, which facilitate Pb ingress.

Compared with other materials described in published literature, those investigated here demonstrate good corrosion resistance in molten lead at high temperatures. Their volumetric heat capacities of 4.7 and 4.5 MJ m^{−3} K^{−1} indicate a high TES capacity, which exceeds that of current state-of-the-art materials.

All samples demonstrated satisfactory performance in corrosion resistance tests.

Based on these findings, further investigation is required prior to implementation in a TES system. In particular, detailed characterization of the thermophysical and mechanical properties is necessary, including thermal cycling corrosion tests, precise determination of the thermophysical parameters, and evaluation of the mechanical stability. Additionally, the selected ceramics should have high purity, as demonstrated in this study, where increased purity correlates with improved performance. The resulting ranking of all analyzed materials, from best to worst (explained and summarized in Table 3), is MgO-3, MgO-1, fused MAS, MgO-2, and Al-rich MAS.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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