C12 Advanced Technologies

Save Time, Money, and Frustration During the Sintering Process

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Nearly everyone involved with firing ceramic materials has run into this problem at some point – a green ceramic part, such as a cast or molded shape, is loaded into a furnace and subjected to a firing schedule that is designed to produce an optimally sintered component. Unfortunately, when the sintered part is removed from the furnace, it has reacted with the firing surface, resulting in sticking, cracking, and contamination. Technical ceramics such as tape cast multilayers, 3D printed structures, components with volatile phases, and other functional materials are especially challenging.

C12 Advanced Technologies provides solutions for sintering the most difficult materials, including PZT/PLZT piezoelectrics, LSM/SOFC fuel cell components, YBCO superconductors, LLZO battery electrolytes, specialty capacitors, and other reactive materials. C12 offers porous and fully dense versions of its patented single-phase MgO setter plates and kiln furniture, as well as specialty coatings for demanding applications that require highly inert ZrO_2 and MgO firing surfaces. C12 high performance products are available today, and you can speak with a knowledgeable product engineer at (206) 795-8925.

As shown in Figure 1a, excellent results can be achieved when setters and firing surfaces are optimally engineered. In sharp contrast, Figure 1b shows what can happen when reactive components are sintered with conventional setter materials.

Figure 1a. PLZT ceramic substrate fired with high-density MgO setters from ***C12 Advanced Technologies***. The as-fired PLZT substrate is flat and crack-free, with almost no out-diffusion of volatile (Pb) components or staining.

Figure 1b. A PLZT ceramic substrate fired with conventional alumina setter and cover plates. The as-fired PLZT substrate shows severe sticking, cracking, and out-diffusion of volatile (Pb) components.

Preventing these expensive and time-consuming mistakes begins with a working understanding of the underlying materials science, including the kinetics of the sintering process and information that can be obtained from resources such as phase diagrams. The most important factors are summarized below:

1. The vapor pressure and diffusion rates of volatile components.

2. The activities and reaction rates of volatile components with firing setters, trays, crucibles and other kiln furniture.

3. The morphology (size, shape) and surface energy of reactive particles, surfaces, and setter powders.

Some specific examples may help to illustrate the concepts.

Alumina (Al_2O_3) ceramics are commonly used for many high temperature processing applications, and alumina kiln furniture is readily available from commercial sources. A materials engineer might therefore consider using alumina setter plates when given the task of sintering lead zirconate titanate (PZT) piezoelectric transducers for a new energy harvesting device. Unfortunately, the PZT composition contains lead oxides that become volatile at relatively low temperatures. During the high temperature sintering process, lead containing species (PbO) are present in the gas phase, and they can react with alumina setters or trays. A close look at the Al_2O_3-PbO phase diagram in Figure 2 shows that the PbO gas phase can react with Al_2O_3 resulting in the possible formation of $2PbO{\cdot}Al_2O_3$, $PbO{\cdot}Al_2O_3$, and/or $PbO{\cdot}6Al_2O_3$.

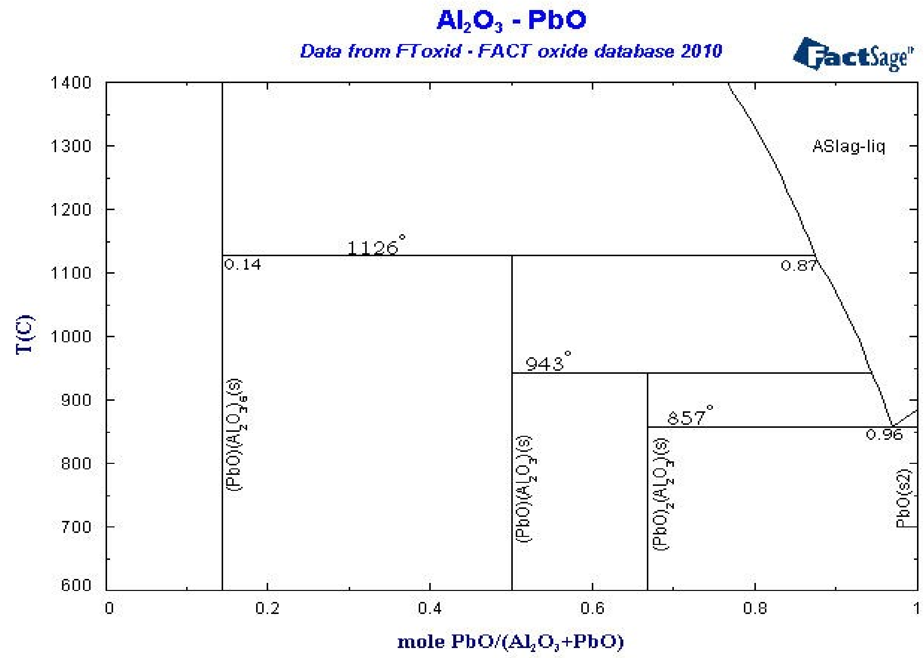

Figure 2. The Al_2O_3-PbO binary phase diagram.

The partial pressure of PbO will determine the type of compound most likely to form. A possible reaction sequence based on the activity of PbO and the formation of lead aluminates is shown in Figure 3. Research has shown that excess PbO in PZT starts evaporating above 575 C, and that PbO bound in the PZT structure begins to volatize above 700 C [1]. The volatile PbO species is adsorbed (chemisorption) onto the surface of the Al_2O_3 setter, and as the sintering temperature is increased, PbO diffuses into the setter and forms lead aluminate phases ($PbAl_2O_4$) at about 760 C. When the temperature reaches the PbO- Al_2O_3 eutectic temperature of 860 C, the $PbAl_2O_4$ phase begins to melt (as shown in the phase diagram). At the peak temperature of about 1200 C, the PZT compact is typically reaching the fully sintered state. As the temperature is decreased, any liquid phases begin to solidify, and there is significant potential for the sintered PZT components to reaction bond with the alumina setter, causing sticking, cracking and warping upon cooling.

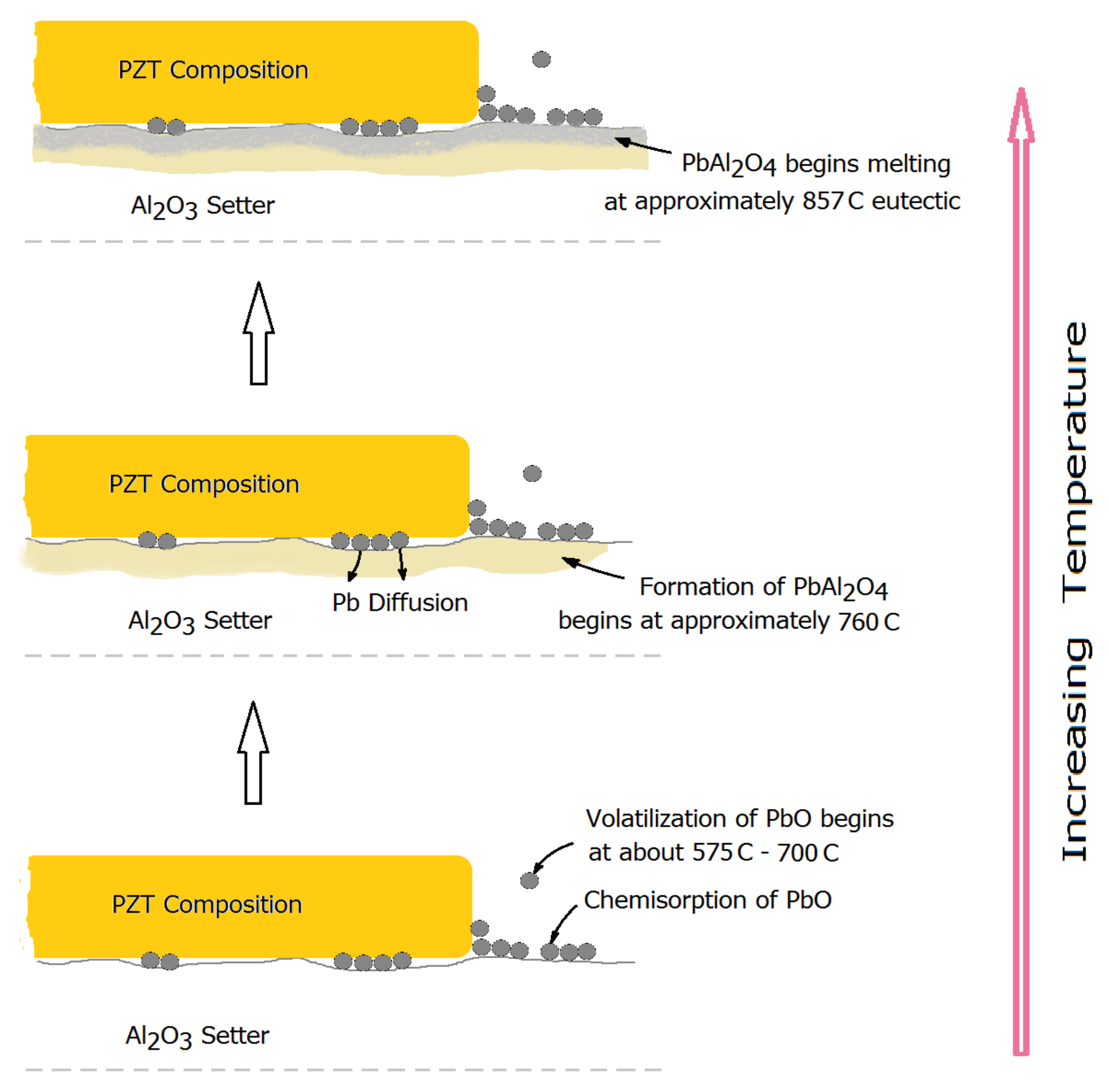

Figure 3. Possible reactions based on the Al_2O_3-PbO phase diagram.

A more satisfactory approach would involve using a setter material that is less likely to react with PZT. Figure 4 shows a portion of the SiO_2-MgO-PbO ternary phase diagram. As can be seen in the lower portion of Figure 4, there are no stable intermediate compounds that form in the binary MgO-PbO system. Additionally, it has been shown that there is no solid solution of PbO in the binary compounds of SiO_2 and MgO, or MgO in the binary compounds of SiO_2 and PbO [2]. This may be a consequence of the large difference between the Mg^{2+} and Pb^{2+} ionic radii, and the close packed MgO crystal structure, which results in immiscibility between these two end members. These factors would all lead to the conclusion that pure MgO will tend to be a non-reactive setter material that is much less likely to cause PZT components to stick or crack. A similar analysis shows that pure MgO substrates should also be highly resistant to Li out-diffusion from LLZO battery electrolytes and many volatile components such as Mn that comprise LSM and SOFC fuel cell compositions.

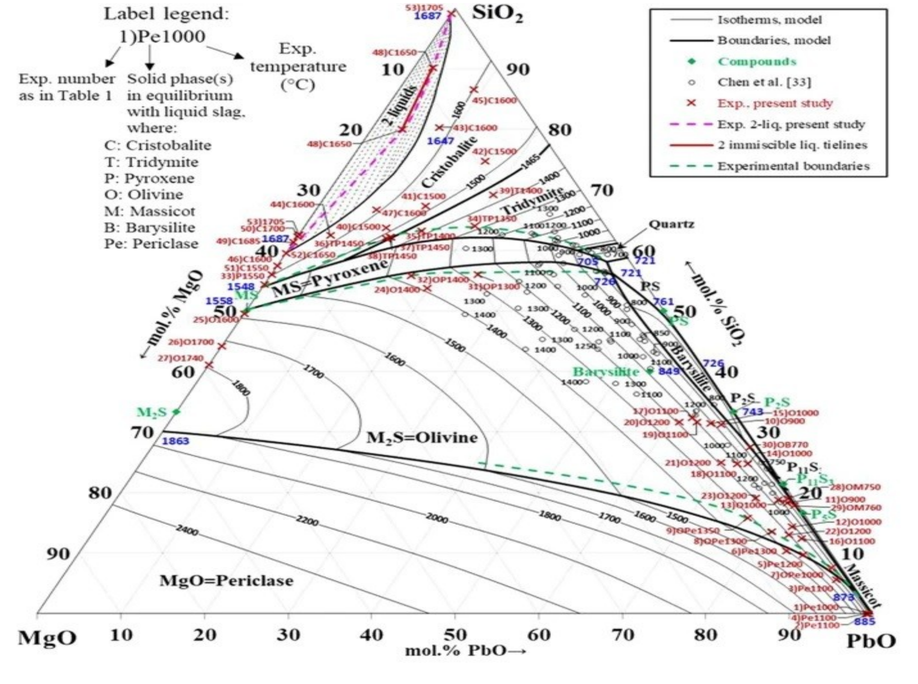

Figure 4. Liquidus surfaces of the PbO-MgO-SiO_2 system [2].

References

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2. Abdeyazdan, H., Shevchenko, M., Hayes, P.C. et al. Integrated Experimental and Thermodynamic Modeling Investigation of Phase Equilibria in the PbO–MgO–SiO2 System in Air. Metall Mater Trans B 53, 954–967 (2022). Open Access, this article is licensed under a Creative Commons Attribution 4.0 International License, https://creativecommons.org/licenses/by/4.0/.