Effect of Lead Oxide Vapor on the Strength of Alumina

By. Abdelaziz Elmadani
Advisers: Professor David J. Green and Professor Zi-Kui Liu

Introduction

Chemical and thermal stability, relatively good strength, thermal and electrical insulation characteristic combined with availability in abundance have made aluminum oxide Al_2O_3 ,or alumina, attractive for engineering applications. Piezo Kinetics Inc. (PKI) located in Bellefonte, PA, manufactures piezoelectric ceramics for a wide range of applications including ultrasonic welders, ultrasonic cleaning machines, sonar devices, surgical cutting tools, and sensors. Lead zirconate titanate (PZT) is one of the company's primary products and its production involves heating powder compacts to high temperature (~1300 C) to densify the material to the final form. It is well known that lead oxide vaporizes from PZT during this sintering process.[1] In order to reduce the lead loss, alumina crucibles are used to cover the PZT sintering bodies. However, during repeated use, the alumina crucibles have been developing cracks. PKI spends an average of $100,000 a year to replace these broken crucibles.[1] It is postulated in the current study that a corrosion reaction is occurring between the PbO vapor and the Al_2O_3.

Background:

It has been observed that the lead oxide that vaporizes from PZT during the sintering process leads to corrosion of the aluminum oxide crucibles that are used to contain this vapor. The mechanism of this corrosive attack is not understood. Thus, the aim of this research is to quantify the corrosion rate and its influence on the strength of the aluminum oxide. In addition, thermodynamic calculations will be performed to determine and characterize the phases involved in the corrosive chemical reaction.

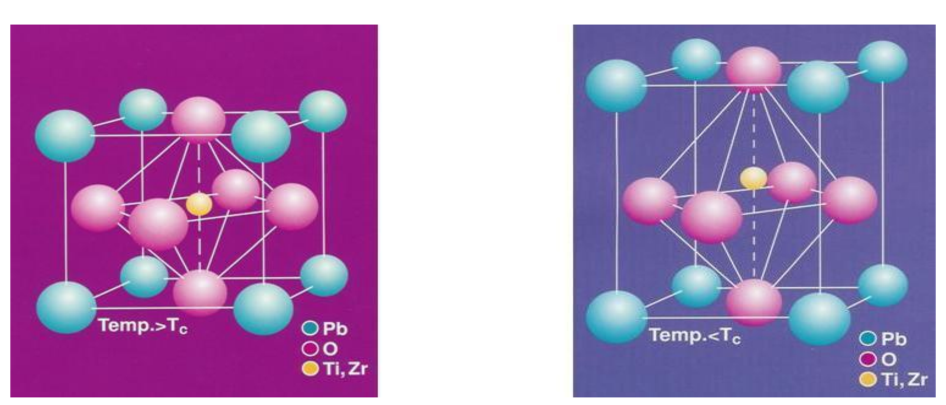

Figure 1. Crystal structure of cubic PZT changes during cooling. The crystal structure of PZT (a) above the Curie point the cell is cubic; (b) below the Curie point the structure is tetragonal with Pb^{2+} and Ti^{4+}/ Zr^{4+} ions displaced relative to O^{2-} ions. [1]

Equations

Density

$$\rho = \frac{m}{V}$$

where, m is the mass and v is the volume

Strength Testing

$$\sigma_f = [(1-\nu)\frac{{D_S}^2 - {D_L}^2}{2D^2} + (1+\nu)\ln\left(\frac{D_S}{D_L}\right)]$$

where F is the breaking load in units of N and is the thickness, D_S is the diameter of the supporting rings, D_L is the diameter of loading ring, D is the diameter of the sample, and ν is Poisson's ratio.

PbO—Al_2O_3 System

Experimental studies on the PbO-Al_2O_3 system have been reported by a number of researchers who have identified three incongruently melting compounds as shown in figure 2. According to Dessureault[6], the compound $Pb_2Al_2O_5$ decomposes in the solid state around 955°C and $PbAl_2O_4$ and $PbAl_{12}O_{19}$ around temperature at 1105 °C and 1511 °C, respectively

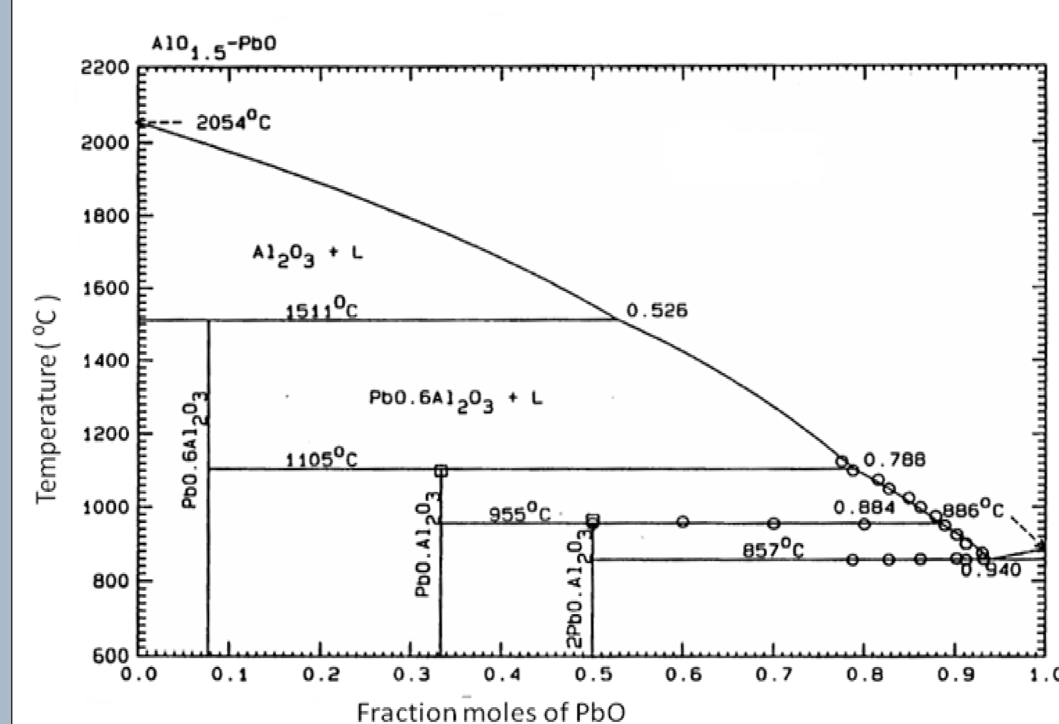

Figure 2. Al_2O_3– PbO phase diagram. [2]

Results and Discussion

Table 1 shows the sound velocity, the density and the calculated Young's modulus for as-received and exposed alumina.

Table 1: Sound velocity, Young's modulus and density values before and after exposure

Material	Sound velocity (km/s)	Density (g/cm³)	E (GPa)	Samples (N)
Al_2O_3 (As-received)	9.278	3.903	285.1	25
Al_2O_3 (Exposed 1)	7.459	3.830	181.0	30

The strength and sound velocity of aluminum oxide decreases when it was exposed to the furnace atmosphere. The sound velocity dropped from 9.278 km/s to 7.459 km/s and the density and Young's modulus seem decrease. The Young's modulus does not agree with the expected properties of Al_2O_3. This is due to the small dimensions of the samples. To solve this problem, a new high frequency commercial tester must be purchased.

Strength Data

Table 2 shows the characteristic strengths of the Al_2O_3 specimens decrease when exposed to lead oxide, where the average strength dropped from 300 MPa to 137 MPa

Material	Mean Equibiaxial Strength (MPa) ± standard deviations		Number of Tests (N)
Al_2O_3 (As-received)	300.2	± 45.8	25
Al_2O_3 (Exposed 1)	136.9	± 25.6	30

Figure 3 shows the Weibull plots of fracture stresses and F, the failure probability

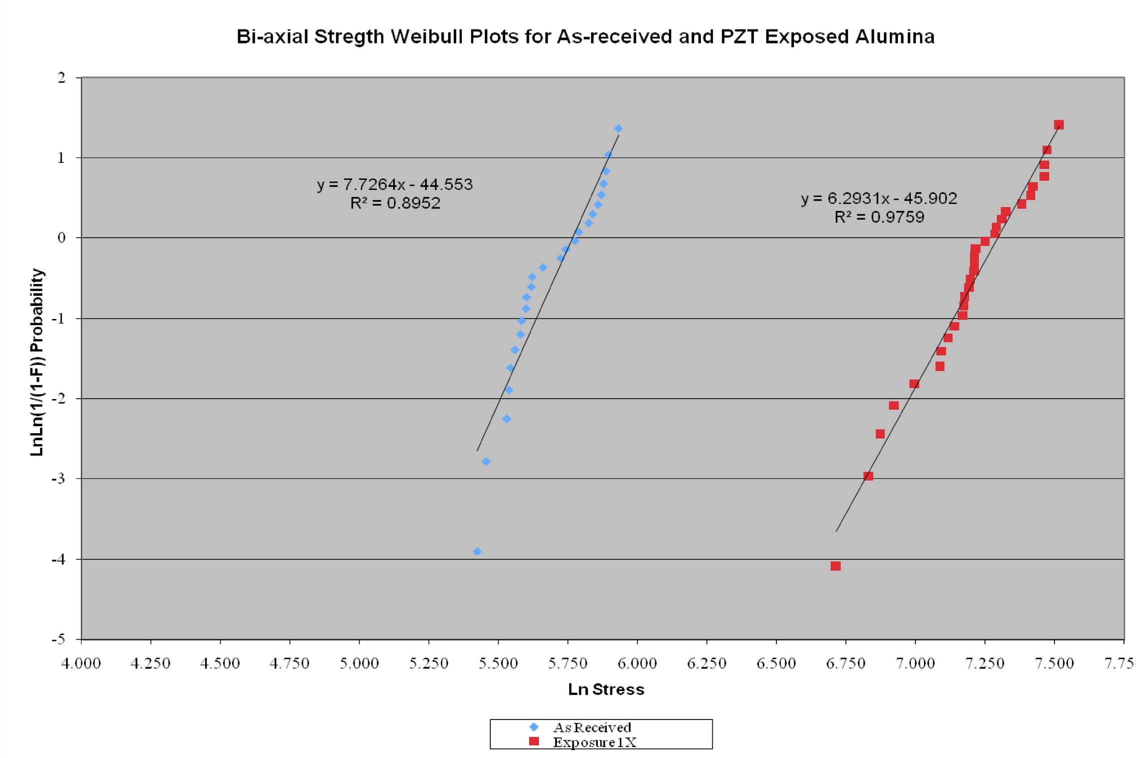

Figure 3: Weibull plot for as-received Al_2O_3 specimens and when exposed to lead oxide vapor in the sintering furnace for PZT production.

Phase Identification

Figure 4 shows x-ray diffraction patterns shows the x-ray diffraction patterns of alumina after lead exposure. The result shows strong peaks of α–Al_2O_3 and at least one peak of beta-alumina. However, it also shows secondary peak of $PbAl_{12}O_{19}$. due to the exposure.

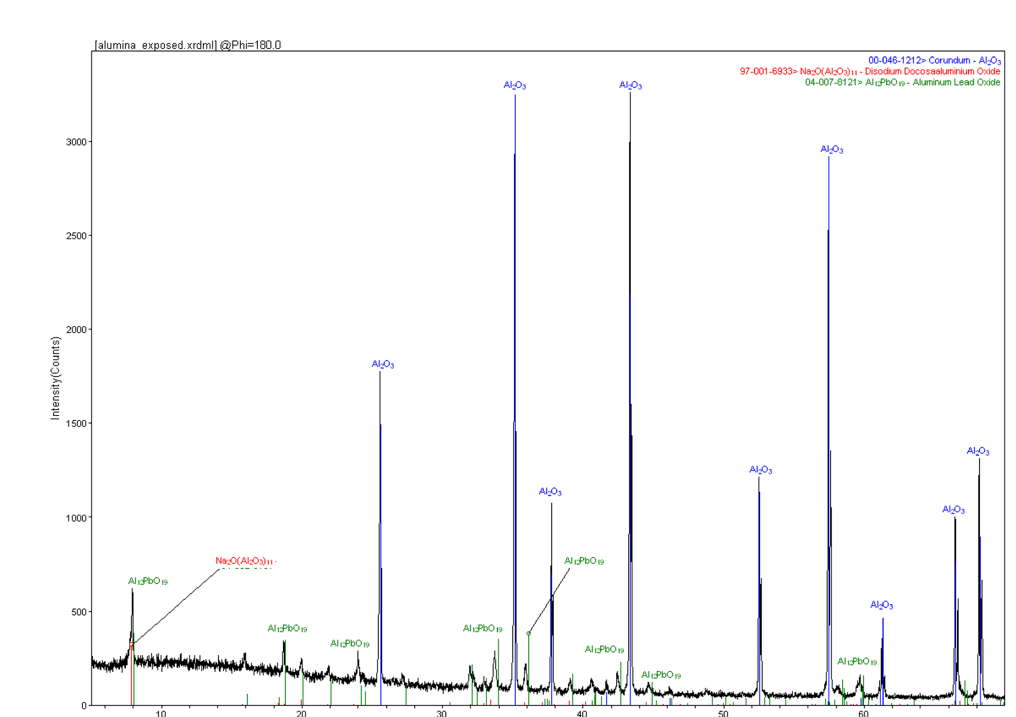

Figure 4: X-ray diffraction patterns of alumina when it was exposed to PZT.

Microscopy

Figure 5 shows SEM micrographs of as-received alumina. The roughness of the surface can be observed in the figures and the material has high density.

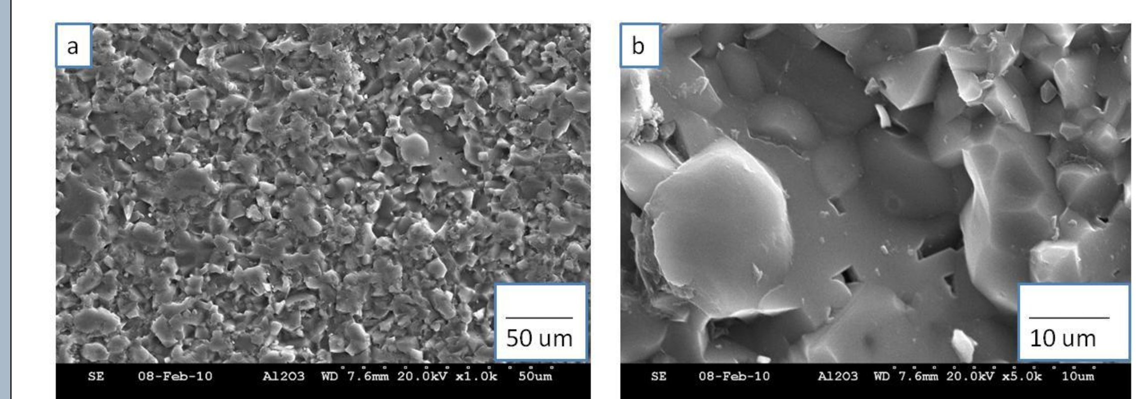

Figure 5. Scanning electron microscope of as-received alumina at different magnifications.

Figure 6 shows SEM micrographs of alumina when it was expose to PZT. Comparatively, the surface of alumina has more porosity present and there appears to be a glassy phase.

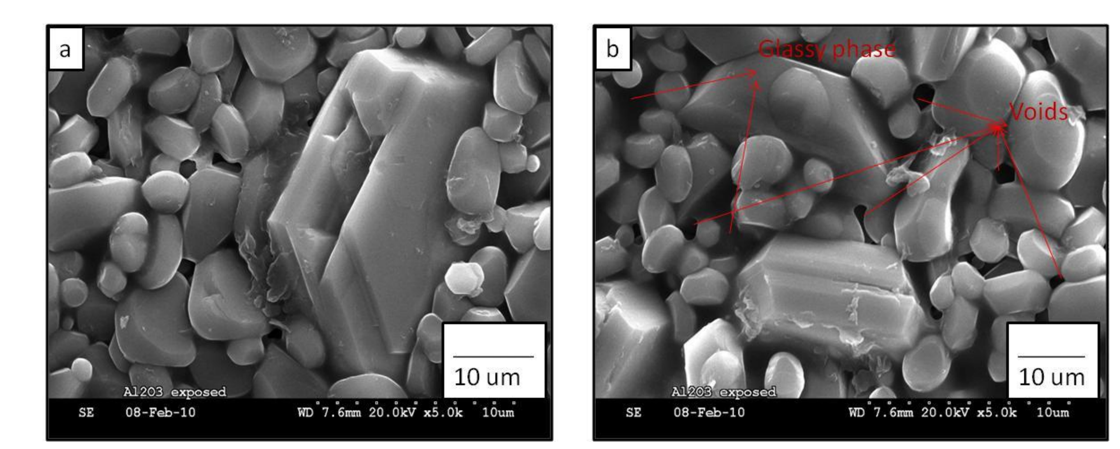

Figure 6. Scanning electron micrographs of porous alumina when it was exposed to PZT at different magnifications showing large grain of lead.

Conclusion:

The strength and sound velocity of Al_2O_3 specimens were decreased when exposed to lead oxide in the sintering of PZT. The phase relations can be extrapolated from the PbO-Al_2O_3 binary diagram. When alumina is exposed to PbO in the sintering of PZT, it shows a three binary compounds $Pb_2Al_2O_4$, $Pb_2Al_2O_5$ and $PbAl_{12}O_{19}$ can be formed. It is concluded that the reaction to form $PbAl_{12}O_{19}$ is most likely. The effect of the PbO vapor on the strength of Al_2O_3 could be results due to a corrosion reaction that produces voids (porosity) present, which can act to concentrate stress. The formations of voids would also reduce the elastic moduli and, hence the sound velocity.

Acknowledgements

Professor David Green, Professor Zi-Kui Liu, Professor Paul Brown, Dr. David Shelleman, Dr. Maria Klimkiewize and Research Assistant Nichole Wonderling

References

[1] S. Dynan, and S. Snyder, Personal Interview (Piezo Kinetics Inc, Bellefonte, PA), January 23, 2009
[2] Y. Dessureault: Ph.D. Thesis, Ecole Polytechnique, Montreal, 1993