Corrosion Behavior of AlN-MgO Composite in High Temperature Lithium Vapor

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Abstract—The corrosion behavior of lithium vapor on AlN composites with three different compositions prepared via plasma assisted sintering in lithium vapor was studied at 550°C. Depending upon the SEM&XRD observations, it is inferred that both MgO and Y₂O₃ have influences on the corrosion resistance of the composites. The presence of Y₂O₃ in the composites can adjust the distribution of precipitation phase on the sample surface while the increased content of MgO contributes to a relatively weak corrosion resistance. Among the three composites, the sample with AlN-25%wt MgO-3%wt Y₂O₃ has the worst corrosion ability.

1. Introduction

Liquid metal batteries are a new type of battery with huge development prospects [1]. Among the liquid metal batteries, a lithium-based system battery is most likely to be commercialized [2][3]. Because of the working temperature and the corrosive vapor generated by the liquid lithium metal, looking for a long-term high-temperature sealed insulating material has become a big problem that must be solved.

Aluminium nitride is an ideal material for long-term high-temperature sealed insulation [4]. When AlN is used as an insulating material, in addition to requiring stronger corrosion resistance, it is usually necessary to connect it to the metal in the liquid metal battery package. In order to avoid possible failure of AlN in liquid metal batteries, an appropriate amount of MgO is added in AlN and the corrosion behaviors of the formed composites are investigated in our present report. Our final objective is to realize good corrosion resistance of AlN in lithium vapor.

2. Experimental

In this experiment, Plasma Activated Sintering (PAS) method was used to prepare samples. First, AlN ceramic powder, Y₂O₃ sintering aid and MgO were weighed according to the required ratio, mixed by a ball grinding mill and dried at 65 °C. Then use a tablet press to pre-compress at 5 MPa, and finally sinter the sample. During the sintering process, the heating rate is 100 °C/min, the pressure is 35 MPa, the holding time is 5 minutes, the sintering atmosphere is nitrogen, and the cooling method is cooling with the furnace.

The thickness of the prepared samples is 3.00-3.10 mm, and the diameter is 25.00-25.50 mm. In order to improve the densification degree of the ceramic sample, we added 3% by weight of Y₂O₃ into the samples. At the same time, in order to adjust the thermal expansion coefficient of the ceramic
samples, we incorporated different proportions of MgO [5]. The composition of the samples is shown in Table 1. Through the comparison of sample 1 and sample 2, analyze the influence of Y$_2$O$_3$. Through the comparison of sample 2 and sample 3, analyze the influence of MgO content on the samples.

Table 1  Proportion of components of the original sample in the experiment

| Sample number | AlN (wt. %) | MgO (wt. %) | Y$_2$O$_3$ (wt. %) |
|---------------|-------------|-------------|--------------------|
| Sample 1      | 85          | 15          | 0                  |
| Sample 2      | 82          | 15          | 3                  |
| Sample 3      | 72          | 25          | 3                  |

The processed sample is fixed in a corrosion container with 304 stainless steel wire. The corrosion temperature of the experiment was set to 550 ℃, and the corrosion time was 4 days, 8 days, 12 days, 16 days, 20 days. Since the elemental metal Li has a very active chemical property, it can react with H$_2$O, O$_2$ and CO$_2$ in the air at normal temperature. Therefore, before the corrosion experiment, the relevant operations on the metal Li are completed in the glove box. During the experiment, Ar was used as the protective gas.

3. Result and discussion

The XRD test was performed on the surface of the samples before and after corrosion. The instrument model used was D8 ADVANCE with a scanning angle of 5° to 80°.

Figure 1. XRD of samples before and after exposure to lithium vapor at 550 ℃ for 4, 8, 12, 16 and 20 days. (a) sample 1, (b) sample 2, (c) sample 3.
The XRD test results of the three samples before corrosion show that all the samples contain a small amount of Al$_2$O$_3$, which should be caused by the introduction of O impurities during the sintering process. The Al$_2$Y$_4$O$_9$ appearing in sample 2 and sample 3 is a typical yttrium aluminate compound produced from the reaction between Y$_2$O$_3$ and Al$_2$O$_3$, which usually exists between the grains and plays a role in improving the densification process of ceramics [6]. Figure 1 also suggests no obvious changes in XRD patterns in spite of corrosion tests at various temperatures.

3.1. Analysis of surface morphology

The SEM photographs of the sample surface before and after corrosion are shown in Figure 2. The instrument model used was SU-8010. During the observation, the voltage was 15 kV and the current was 10 μA.

![SEM photographs of the sample surface before and after corrosion](image)

Figure 2. Surface morphology of samples before and after exposure to lithium vapor at 550 °C for 20 days

After the corrosion, the surface morphology of the samples changed significantly, and granular products appeared on the surfaces of the three samples to varying degrees. By making effective comparison, it is easily found that the surface morphology of sample 1 is very similar to that of sample 3. But, the average size of granular products in sample 3 is relatively less. The surface morphology of sample 2 suggests the presence of Y$_2$O$_3$ in AlN ceramic seems to be able to realize the uniform distribution of the precipitated granular products. Further EDS mapping data of the sample surfaces are given in Figure 3. Figure 3 shows the main component of the granular products is O. Because the oxygen is gaseous at normal temperature, it is speculated that the particles should be the compound contains O element. Due to the difficulty to check the Li element, it is deemed that the granular products on the sample surfaces might be complicated lithium oxide.

![EDS mapping data of sample surfaces](image)

Figure 3. EDS map analysis of the sample surface after exposure to lithium vapor at 550 °C for 20 days
3.2. Analysis of Corrosion Layer

Figure 4 is the fracture morphology of samples before and after corrosion. By comparison, it can be seen that the fracture of the original sample is grayish white, and with the extension of the corrosion time, the color of the fracture gradually deepens and eventually turns black.

![Figure 4](image)

Among them, sample 1 can clearly see the existence of the corrosion layer when it is corroded for 4 days, 8 days, 12 days, and 16 days, and the entire section has become black after 20 days of corrosion. The macro morphology of the fractures of samples 2 and 3 after being corroded in lithium vapor is similar to that of sample 1. But, the sample 3’s structural corrosion is becoming more and more serious with the extension of the corrosion time. This shows that under the same corrosive environment, sample 3 is not as capable of maintaining its own structure as sample 1 and sample 2.

![Figure 5](image)
Figure 5 is the photographs of the sample fractures with a magnification of 3000 X. After 20 days of corrosion, it can be clearly seen that there is a gap between the outer layer and the substrate of the samples. The thickness of the outer layer of the sample 1 is 2 μm while that of the sample 2 is 6 μm, which is significantly thicker than that of the sample 1. This phenomenon suggests that the depth of Li vapor penetrating into the sample 2 is deeper. So it can be considered that sample 1 has stronger corrosion resistance to metal Li vapor under the similar conditions.

It’s reported that Y₂O₃ can react with native Al₂O₃ initially exists in the AlN powder, and promote liquid phase sintering of AlN by forming yttrium aluminium compound on the grain boundary [6]. These yttrium aluminium compounds can further react with lithium forming some brittle phases, which lower the corrosion resistance of the composites. This might be a key factor which can be used to explain why sample 1 is superior to sample 2 in corrosion resistance.

Figure 6. Cross-sectional morphologies of samples before and after exposure to lithium vapor at 550 ℃

The SEM paragraphs with low magnification (Fig. 6) suggest the fracture morphology of sample 3 is destroyed seriously, and large amounts of the corrosion layer has fallen off the matrix after corrosion, so the corrosion layer of sample 3 cannot be observed clearly in Figure 5.

Generally speaking, the strength of composite ceramics depends to some extent on the uniformity of the distribution of dopants in the matrix. When the MgO content is approached to 25wt.%, agglomeration of MgO in the AlN matrix is easy to form and might result in stress concentration, which will result in possible stress corrosion and decreased corrosion resistance of composite.

4. Conclusion
In this paper, the corrosion behavior of lithium vapor on AlN composites with three different compositions prepared via plasma assisted sintering in lithium vapor was studied at 550°C. The results reveal that both MgO and Y₂O₃ are harmful to the corrosion resistance of the composite in the lithium vapor environment.

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