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電磁浮遊炉を用いた直接観察による Al-Mg 合金の酸化皮膜挙動の解明

In-situ Observation of the Destruction of Oxide Layer on Al-Mg Alloys Using Electromagnetic Levitation

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1. Introduction

In brazing aluminum alloys, maintaining an oxide-free surface is crucial for optimal process performance. Although fluoride-based fluxes can achieve such a surface, the post-braze removal of residual flux is inefficient, consuming excessive time and resources. It has been reported that adding a small amount of magnesium to Al-Si brazing alloys enables flux-free brazing, though not optimally. This improvement is believed to result from the reduction of the Al_2O_3 oxide layer formed on the surface of molten brazing filler alloys by the addition of magnesium. Our group recently proposed a novel perspective on the role of added magnesium: it leads to the formation of $\text{MgAl}_2\text{O}_4(\text{s})$ at the surface of the filler alloys, which induces shrinkage stress that allows the oxide layer to crack and fragment due to the different densities of $\text{MgAl}_2\text{O}_4(\text{s})$ and $\text{Al}_2\text{O}_3(\text{s})$.

In this study, we employed electromagnetic levitation (EML) to melt aluminum alloys with added magnesium, facilitating in-situ observation of oxide layer destruction. The primary objective was to validate our hypothesis regarding the mechanism of oxide layer destruction and to further investigate the effects of magnesium addition.

2. Experimental procedure

A cube of Al-Mg alloy sample was chemically cleaned using an aqueous solution of fluoride nitrate in an ultrasonic cleaner and then placed on a quartz holder inside the EML chamber. The atmosphere within the chamber was replaced with a high-purity Ar-He gas mixture, maintaining an oxygen partial pressure of approximately 10^{-2} Pa. The sample was electromagnetically levitated and melted under the gas flowing at 2L/min. The behavior of the oxide layer forming on the molten droplet was monitored using a high-speed video camera operating at the frame rate of 500 FPS. Some samples were quickly solidified and collected before the oxide layer could be destroyed.

The collected sample was maintained in an iodine-methanol solution heated to 60 °C for two hours. During this period, the solution was stirred continuously to ensure the selective dissolution of the metal portion only.

The phase constitution of the residual oxides was then analyzed using transmission electron microscope (TEM).

3. Results and Discussion

Figure 1 shows typical time-lapse images that capturing the progress of the destruction of the oxide layer on the surface of a molten Al-Mg alloy sample levitated by EML. The levitated sample melted into a spherical shape, still covered by the oxide layer formed during heating. (Fig. 1a). A white phase is observed in several locations on the surface of the gray oxide layer. Furthermore, some white phases expand instantaneously during the heating of the sample, as indicated by the dashed circle in Fig. 1b. A crack appears from this white phase, followed by rapid disappearance of the oxide layer (Fig. 1c).

Electron diffraction analysis using TEM confirmed the presence of $\text{MgAl}_2\text{O}_4(\text{s})$ together with $\text{Al}_2\text{O}_3(\text{s})$ in the oxide layer. Given the higher emissivity of $\text{MgAl}_2\text{O}_4(\text{s})$ compared to that of $\text{Al}_2\text{O}_3(\text{s})$, it is reasonable to suppose that the white phase is $\text{MgAl}_2\text{O}_4(\text{s})$. This behavior aligns with our hypothesis that the addition of magnesium induces shrinkage stress, causing the oxide layer to crack and fragment due to the different densities of $\text{MgAl}_2\text{O}_4(\text{s})$ and $\text{Al}_2\text{O}_3(\text{s})$.

This destruction behavior of the oxide layer from $\text{MgAl}_2\text{O}_4(\text{s})$ is in consistent with our hypothesis that adding magnesium to the aluminum alloys induces shrinkage stress that allows the oxide layer to crack and fragment due to the different densities of $\text{MgAl}_2\text{O}_4(\text{s})$ and $\text{Al}_2\text{O}_3(\text{s})$.

To explain the rapid disappearance of the oxide layer after cracking, we delve into the possibility of gas formation reactions from the melt. When the oxide layer completely covers the melt surface, gas phase formation reactions are kinetically inhibited. However, once a gas-liquid interface appears due to cracking, these reactions become possible. The high vapor pressure of magnesium in the alloy may lead to its evaporation, followed by the formation of $\text{MgO}(\text{s})$ with oxygen gas present as impurities in the atmosphere. This process reduces the oxygen partial pressure in the vicinity of the melt surface, facilitating the reduction of the oxide layer. The formation of $\text{Al}_2\text{O}(\text{g})$ through the following reaction further promotes the disappearance of the oxide layer.

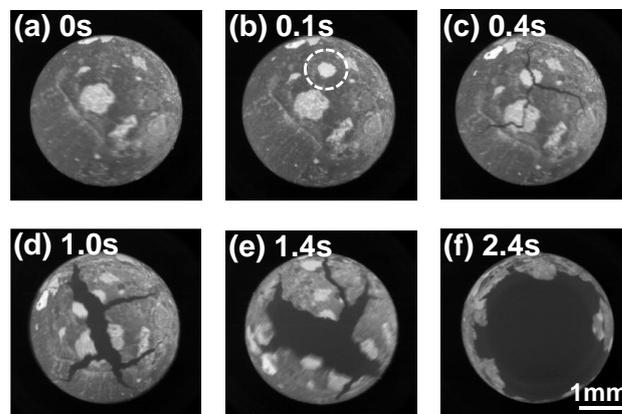
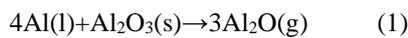


Figure 1. Time-lapse images of oxide layer destruction on molten Al-Mg Alloy sample levitated by EML.

4. Summary

We observed the destruction process of the oxide layer on an Al-Mg alloy sample over using EML. The rapid expansion of white phases during heating led to cracking in the gray oxide layer, followed by its swift disappearance. Electron diffraction analysis confirmed the formation of $\text{MgAl}_2\text{O}_4(\text{s})$ and $\text{Al}_2\text{O}_3(\text{s})$ within the oxide layer. This research supports the mechanism by which the addition of magnesium contributes to the formation and destruction of cracks in the oxide layer.

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References

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