# Surface films formed on the intermetallic $Al_3Mg_2$

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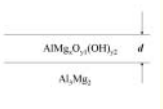
## The aim of the project is to study the initial film formed in water on $Al_3Mg_2$ by XPS and ToF-SIMS

### Experiment:

- The sample was mechanically grinded to 4000 grit SiC paper without water. In some case, the surface were further polished to ¼ μm with diamonds.
- The grinded sample was then exposed to ultra pure water during 30, 30, 60 and 300s. XPS experiments have been carried out after each steps of immersion. ToF-SIMS analysis were also processed on the polished sample after certain time immersion.

## XPS on grinded $Al_3Mg_2$ after immersion in ultra pure water




**Layer thickness and composition calculated from :**

$$I_{Mg} = KA(\theta)\sigma_{Mg}\lambda_{Mg}^{1}T_{Mg}D_{Mg}^{1}\sin\theta\exp\left(-\frac{d_{oxide}}{\lambda_{Mg}^{oxide}\sin\theta}\right)$$

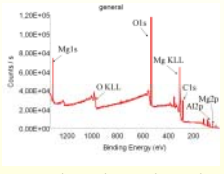
$$I_{Mg^{2+}} = KA(\theta)\sigma_{Mg}\lambda_{Mg}^{oxide}T_{Mg}D_{Mg}^{oxide}\sin\theta\left(1-\exp\left(-\frac{d_{oxide}}{\lambda_{Mg}^{oxide}\sin\theta}\right)\right)$$

$$I_{Al} = KA(\theta)\sigma_{Al}\lambda_{Al}^{1}T_{Al}D_{Al}^{1}\sin\theta\exp\left(-\frac{d_{oxide}}{\lambda_{Al}^{oxide}\sin\theta}\right)$$

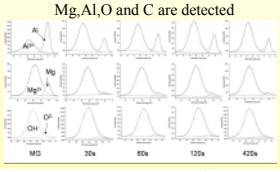
$$I_{Al^{3+}} = KA(\theta)\sigma_{Al}\lambda_{Al}^{oxide}T_{Al}D_{Al}^{oxide}\sin\theta\left(1-\exp\left(-\frac{d_{oxide}}{\lambda_{Al}^{oxide}\sin\theta}\right)\right)$$

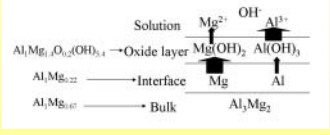
$$I_{O} = KA(\theta)\sigma_{O}\lambda_{O}^{oxide}T_{O}D_{O}^{oxide}\sin\theta\left(1-\exp\left(-\frac{d_{oxide}}{\lambda_{O}^{oxide}\sin\theta}\right)\right)$$

σ : cross section of photoionisation, depending on the element and the level studied
λ : the attenuation length, depending on the element and the level studied
T : transmission factor depending on the element and the level studied
Θ : the take-off angle describe on the left
D : density of the element in the sample
K : a constant link to the machine
A : aera analyzed




Mg,Al,O and C are detected

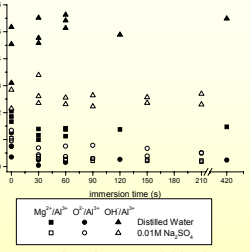



- The metallic Mg oxidized faster than metallic Al ($Al_1Mg_{0.22}$);
- The $Al(OH)_3$ dissolve faster than $Mg(OH)_2$ ($Al_1Mg_{1.4}O_{0.2}(OH)_{5.4}$);
- The thickness is around 10nm.

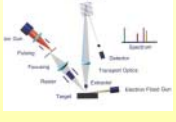
## XPS on grinded $Al_3Mg_2$ after immersion in 0.01M $Na_2SO_4$ solution

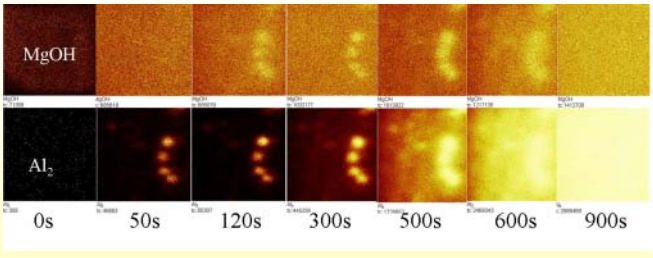
| | Neutral pH | Saturated with $Mg(OH)_2$ |
|---|---|---|
| De-aerated ultra pure water | $Al_1Mg_{1.3}O_{0.2}(OH)_5$ / $Al_1Mg_{0.35}$ | $Al_1Mg_{1.05}O_{0.2}(OH)_5$ / $Al_1Mg_{0.32}$ |
| 0.01M $Na_2SO_4$ | $Al_1Mg_{1.2}O_{0.2}(OH)_{5.2}$ / $Al_1Mg_{0.3}$ | $Al_1Mg_{1.22}O_{0.2}(OH)_{5.5}$ / $Al_1Mg_{0.21}$ |

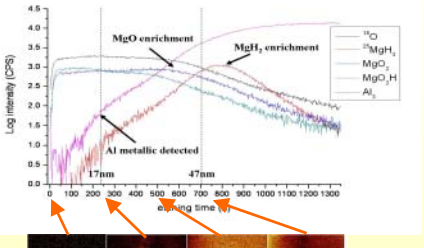



- As the metallic peak is very small, the ratio between Al and Mg could be less accuracy, here it can be conclude that no significant difference.
- The result among ultra pure water, de-aerated ultra water and de-aerated ultra pure water with saturated $Mg(OH)_2$ do not have big difference.
- The pH value between neutral and 10.5 do not have much effect on the layer composition
- Dilute $Na_2SO_4$ could make less Mg in the layer (or more Al) and more $O^{2-}$. After addition of $Mg(OH)_2$, the Mg become more less (or more enrichment of Al). That means the corrosion of Mg is very sensitive with the sulfate ions in solution.

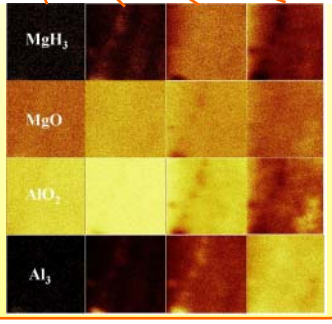
## Time of flight SIMS (ToF-SIMS) study on Polished $Al_3Mg_2$






ToF SIMS sputtering image and profile curve on polished $Al_3Mg_2$ after 30 min immersion in ultra pure water

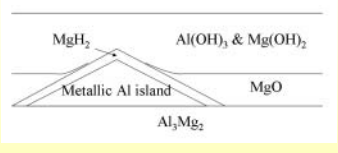



- The TOF-SIMS data confirm the metallic Al island on the surface after immersion in the ultra pure water.
- The hydroxide is more rich in the outer layer and oxide is more rich in the inner layer.

From the sputter image, the enrichment of MgOH signal is likely the same location with metallic Al islands. Which might contributed from the metallic Mg under that or MgO surrounding that.

- From the profile image, the $MgH_2$ signal first enrich in the metallic Al island area then get lack, which means the $MgH_2$ could formed on the surface of metallic Al island.
- These islands are μm in area but nm is height.

## Evolution of layer structure and composition on $Al_3Mg_2$ after initial immersion




- Most of the initial layer formed in the solution on the $Al_3Mg_2$ surface is hydroxide layer, especially the outer part;
- There is metallic Al island at the interface due to the selective corrosion of metallic Mg. These islands are μm in area but nm is height;
- The metallic Al island were covered with a thin layer of $MgH_2$. Between the island, there is a relatively enrichment of MgO close to the interface.

## Conclusions

- The surface film formed on $Al_3Mg_2$ after immersion is the mixture of hydroxide and oxide of Mg and Al. The film contain less $Mg(OH)_2$ in 0.01M $Na_2SO_4$ solution, while the $Mg(OH)_2$ saturated enviroment do not affect the layer composition much.
- The layer thickness on grinded $Al_3Mg_2$ is around 10nm and stable at first few minutes immersion. The polished $Al_3Mg_2$ has interface around 47 nm deep from the surface.
- The metallic Al island were found on the interface of $Al_3Mg_2$ as the result of selective corrosion of Mg. The $MgH_2$ were found cover the surface of those islands and MgO were rich in the inner layer.