Decomposition and Reaction of Thermal-Formed Alumina in Aluminum Alloy Castings

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Oxide films are readily entrapped in aluminum alloy castings during the melting, pouring or filling process resulting in defective geometry or quality. The entrapped oxide films may be of different shapes and/or composed of varying constituents (or oxides). It is extremely difficult to directly produce a given type of oxide film with a given thickness, from the aluminum alloy melt. Aluminum alloy castings have a thermally formed oxide film on their machined surface after being heated. In this study thermally formed aluminum oxide samples were produced from pure aluminum. The intend is to investigate the reaction and decomposition of this oxide in aluminum alloy melts. The reactions of the thermally formed aluminum oxide with aluminum-silicon and aluminum-magnesium alloys are discussed.

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1. Introduction

Aluminum is a very active metal when it comes into contact with air or oxygen. Consequently, an oxide film will be deposited on its surface during heating. After melting, this oxide film may be entrapped in the melt as well as in the casting. Several researchers have studied the thermal oxidation of aluminum and have found that an air-formed oxide film develops when aluminum is heated in air or oxygen at temperatures above 723 K. Initially an amorphous oxide film is formed and then γ-Al2O3 crystals develop at the metal-oxide interface.1–4) Upon increasing the oxidation temperature, a gradual transition from the amorphous aluminum oxide to the crystalline γ-Al2O3 occurs via the inward diffusion of oxygen. Shimizu used TEM to confirm the apparent induction period for γ-Al2O3 development via the thermal oxidation of Al.5)

Oxide film and oxide inclusions are readily trapped in Al alloy castings. They significantly affect the properties of the castings. The alloying elements Si and Mg are commonly added in the alloys to improve the fluidity and/or the mechanical properties of the alloy castings. These elements also increase the number of inclusion trapped in the melt during the degassing process which results in a high pore count in the solidified castings.6–8) Silicon and magnesium interact with the oxide film in the melt, but such an interaction has rarely been studied experimentally and reported. In Whangbo’s study, an Al prelayer was deposited on a Si substrate at room temperature and then the Al2O3 deposition process was carried out. A polycrystalline Al2O3 film grew at 973 K. He found that Al diffused at the interface of the Al2O3 and Si.9) He further found that the Al2O3 film that grew on the oxidized Si surface showed a more abrupt interface between Al2O3 and Si than the oxide film that grew on a clean Si substrate.10) Saito also confirmed that the crystalline SiO2 accelerated the transformation of γ-Al2O3 to α-Al2O3, and SiO2 could act as a heterogeneous nucleation site.11)

Yang pointed out that in the Direct Melt Oxidized processing of aluminum alloys (DIMOX), silicon and magnesium are indispensable for the oxidation process to take place and silicon is more effective than magnesium in accelerating this process.12) He proposed two reactions:

\[
1[\text{Mg}] + 1/2(\text{O}_2) - 1[\text{MgO}] + \frac{1}{4}[\text{Al}_2\text{O}_3] + 2/3[\text{Al}],
\]

\[
\frac{1}{4}[\text{Mg}] + 2/3[\text{Al}_2\text{O}_3]
\]

where the symbols \{ \}, ( ) and [ ] represent the liquid, gas and solid states, respectively. A small amount of Mg is sufficient to cause the continuous growth of Al2O3 to take place. For silicon, the liquid Al reacts with SiO2, which is formed by the oxidation of Si. The reaction can be expressed as follows:

\[
3[\text{Si}] + 3(\text{O}_2) - 3[\text{SiO}_2] + 4[\text{Al}] - 3[\text{Si}] + 2[\text{Al}_2\text{O}_3]
\]

According to his observations, a larger amount of Si is needed in the above reaction and for the growth of Al2O3 in the melt.

Cao et al. discovered that Al2FeSi in Al–Si alloys would precipitate on the wetted outside surface of a thin alumina film.13) Mohanty et al. observed a similar result, where aluminum inclusions had engulfed by silicon after the A356 alloy had solidified.14) Silicon in aluminum alloys may interact with alumina but this interaction has been rarely discussed. In this study the intention is to produce a thermal oxide with a high purity Al sample and to investigate the reaction and decomposition of this oxide in aluminum alloy melts. Samples were placed in contact with different Al alloys, then heated and held in a molten condition for a period of time. The thermal oxide layer would grow in thickness, then fractured or be decomposed as affected by the silicon and/or magnesium in the Al alloys.
2. Experimental Procedure

The materials used in this study included high purity Al (5N:99.999%), Al–7%Si, Al–13%Si, Al–0.5%Mg and A356.2 alloys. They were machined to 10 × 10 × 10 mm cubes. A high purity Al cube was polished on one surface by abrasive paper (3M 734 p400). This cube was then heated in a muffle furnace at 883 K for 9 × 10^4 s. Thermal oxide films formed on all surfaces of the heated cube. The oxide film on the polished surface was selected and treated as a reference. This high purity Al cube with the reference thermal oxide film was used as a base metal/oxide film reference (BM/oxide film).

Cubes made of different alloys were each polished on one surface by abrasive paper (3M 734 p400). A cube was set on the BM, with the polished surface in contact with the reference thermal oxide. The whole set of samples was placed on a stand made of a steel block. The stand with the sample was put in a cylindrical pipe, then covered with refractory fibers, as shown in Figs. 1(a) and (b). The air in the heating chamber was pumped out and it was then refilled with Ar gas. The whole set of samples was then heated at 1023 K for a period from 600 to 1200 s. After heating, the sample was cooled in the heating chamber then moved out for sectioning and microscopic observation. The entire sample might not be completely fused if the heating time was not long enough. The fused samples were bound with resin then sectioned in a direction perpendicular to the oxide film. The sectioned sample was polished and removed for optical and SEM observations along with an element mapping analyses.

3. Results and Discussion

In the experiments, a polycrystalline Al₂O₃ film was deposited on the polished surface of the high purity Al cubes (99.999 mass%) after being heated at 883 K for 9 × 10^4 s. The Al and Al₂O₃ interface and the free surface of the Al₂O₃ were bumpy (see Fig. 2). The thermally formed oxide layer was 0.8–1 μm in thickness.

When aluminum is heated in air (or oxygen) over 723 K, amorphous thermal oxide is formed. The γ-Al₂O₃ phase then develops at the amorphous oxide-metal interface by the inward diffusion of oxygen, after which the γ-Al₂O₃ nucleates from the Al-oxide interface via the reaction of inward diffusion of oxygen and aluminum.1–4) Subsequently a limited thickness of polycrystalline γ-Al₂O₃ forms during the thermal oxidation period. Aluminum diffuses continuously to react with the inward diffusion of oxygen to grow γ-Al₂O₃ grains. The SEM observations indicated that the thermal-formed oxide film contained mostly fine γ-Al₂O₃ grains associated with 0.1 μm pores that run through the thermal oxide film (see Fig. 2). The surface layer is obviously rich in oxygen far greater than the stoichiometric Al₂O₃ concentration, probably because of the fine Al₂O₃ grains associated with 0.1 μm pores in the cavities of the pores (see Fig. 2). The ratio of oxygen to aluminum for the thermal oxide film decreases following the increase of the sputtering time or the depth. This high purity Al cube...
deposited with a thermal oxide film was then treated as a base metal (BM), to be sandwiched between cubes of different alloys.

3.1 BM/oxide film reacting with another BM/oxide film
Two BM/oxide film cubes were placed in contact with the oxide films and heated to 1023 K. After heating for 780 s, the whole sample was cooled in the chamber then removed for sectional observation. Figure 5 shows that the $\gamma$-Al$_2$O$_3$ film fractured at some area initiating the Al melt to erupt from the bottom melt.

As explained previously, the thermal oxide on the surface layer is rich in oxygen. When two cubes were stacked together and heated (Fig. 6(a), Al(s) represents the solid Al sample) the thermal oxide film grew slightly via the diffusion of oxygen from the interface, most likely by passing through the micropores (see Fig. 2). Some pores may be sealed due to their critical size and the growth of alumina due to heating. Gas (a mixture of air and Ar) can then be trapped in the micro-channels. When the sample was persistently heated, therefore, any entrapped gas will expand in volume increasing the pressure in the micro-channels. If a sealed micro-

![Fig. 3 ESCA tested result on the first layer (top surface) of thermal oxide film, pure Al heated at 883 K for 25 h.](image3)

![Fig. 4 Relation of tested Al 2p and O 1s versus sputtering time, pure aluminum heated at 883 K for 25 h.](image4)

![Fig. 5 Decomposition of BM/oxide film and BM/oxide film heating at 1023 K for 780 s, (a) SEM photograph, (b) Al mapping, (c) O mapping.](image5)
channel is heated to 1023 K, the gas pressure in the channel may increase up to 0.2–0.3 MPa (2–3 atm). In addition, the great difference in thermal expansions between aluminum and alumina ($\text{Al} = 24.5 \times 10^{-6} \degree C^{-1}$; $\text{Al}_2\text{O}_3 = 8 \times 10^{-6} \degree C^{-1}$) generates tensile stress, which acts on the thermal oxide film during heating. When an oxide film is subjected to tensile stress, micro-cracks may be initiated at the pores within which a great internal pressure to build up (Fig. 6(b)). Those micro-cracks may in time coalesce to form cracks in the film. This reduces the gas pressure in the crack but increases the volume of the gas.

After the samples are melted, as indicated by $\text{Al}_{(m)}$, the entrapped gas tends to float up as bubbles if the gas in the crack reaches a critical size, since the buoyant force is proportional to the volume of gas phase. Alumina can not be wetted with aluminum. A layer of alumina might form at the open gate of the crack (see appendix I(b)). After the gas incubates for a period of time, it reaches a critical size as the micro-cracks coalescence. The gas escapes from the cracks as bubbles that float upward, generating a stream that moves up to fracture the film. Therefore, molten Al that erupted from down in the melt moves upward to fracture the oxide film as shown in Fig. 5. The alumina oxide film becomes decomposed in the melt and fractures into pieces.

### 3.2 Al–XSi reaction with the BM/oxide film

An Al–7%Si alloy cube with one polished surface was placed in contact with a BM/oxide film (down side) and heated at 1023 K for 1200 s. Figure 7 indicates that the thickness of oxide film grew to 3–5 μm, compared to 1 μm for

![Fig. 7 Reaction of oxide film in the experiment of BM/oxide film in contact with polished Al–7%Si cube, (a) SEM photograph, (b) Al mapping, (c) O mapping, (d) Si mapping.](image)

### Fig. 6 Schematic illustrations of reaction of oxide film in experiment, BM/oxide film in contact with BM/oxide film, (a) before heating; during heating, (b) the upper side of cube is solid, (c) the upper side of cube is melted, (d) the lower side of cube is melted.
the pure Al cube, as shown in Fig. 2, and 2–3 \( \mu \text{m} \) for the sample produced from two pure Al cubes as in Fig. 5. Although the lower side of the BM consisted of high purity Al (99.999%), after heating (melting) Si plates showed up on the lower side of the sample (Fig. 7). The eutectic of the Al–7%Si alloy in the sandwich sample melted first. As explained previously, micro-cracks were initiated from the micro-pores. When these micro-cracks came into contact with the eutectic melt, the melt would protrude slightly into the micro-cracks. However the melt could not wet the wall of the micro-cracks (aluminum oxide). Instead, reaction (2) occurred at the opening gate of micro-cracks; appendix I(c), and formed a reacting layer over the micro-cracks. These reacting layers could seal the open gates of the micro-cracks but the cracks could be again formed, since heat was still being supplied. The reacting layers (Si or silica associated with alumina) penetrated into the thermally formed aluminum oxide, step by step, via the micro-cracks. The aluminum oxide film significantly increased in thickness, but was eventually decomposed by the intrusion of reaction products. Figures 7(a) and (c) (O mapping) show that the oxide film was still sound, without apparent fractures. This indicates that the fracture modes of thermally formed aluminum oxide in a pure Al melt and in an Al–Si melt are different. In the former case fracturing occurs due to the evolution of gas bubbles which introduced a stream entering the crack but in the latter it is caused by the decomposition due to intrusion of reaction products (Si or silica with alumina). Consequently, the Al–Si melt penetrated into the oxide film and wended its way down into the pure Al melt (down side) via the existing diffusion channels (i.e., micro-cracks).

Yang has explained that a large amount of Si is needed to accelerate the Al\(_2\)O\(_3\) oxidation process from an aluminum alloy melt.\(^\text{12}\) This indicates that an Al–13%Si melt has a thicker reactive oxide film than does an Al–7%Si melt. Our experimental results indicated that in the Al–13%Si alloy sample the thermally formed aluminum oxide film increased in thickness to 8–12 \( \mu \text{m} \), which is far greater than the 3–5 \( \mu \text{m} \) at the Al–7%Si alloy sample shown in Fig. 7. During heating, in the Al–13%Si alloy more eutectic melt was generated to go into the micro-cracks than in the Al–7%Si alloy, which accelerated reaction (2) in the channels and correspondingly increased the oxide film thickness.

Figures 8(a) to (d) schematically illustrate the developments and the reactions which occurred during heating, where Al–XSi\(_{\text{mol}}\) and Al–XSi\(_{\text{solid}}\) represent the molten and solid Al–XSi alloys respectively. The upper sample is the Al–X%Si alloy with a dry polished surface, Fig. 8(a). A thin oxide film formed on surface during heating, Fig. 8(b). The eutectic in the upper alloy cube melted first. The oxide film at the interface retained its shape, since its melting temperature is far greater than that of the aluminum alloy. The eutectic melt in the upper side of the melt was in contact with the open micro-crack gates caused reaction (2). This reaction persistently occurred at the micro-cracks within the oxide film to form the reacted products. The thermally formed aluminum oxide layer therefore increased in thickness but gradually decomposed in the Al–Si melt via reaction (2) and the silicon particles and/or silica dispersed within the oxide film, Fig. 8(c).

### 3.3 Al–0.5%Mg reacting with BM/oxide film

Figure 9 shows a section of the solidified sample, after the BM/oxide film was placed in contact with the Al–0.5%Mg alloy cube and heated at 1023 K for 900 s. The thermal oxide film increased its thickness to 2–5 \( \mu \text{m} \), judging from the distribution of oxygen intensity, Fig. 9(c). Figures 10(a) to (d) schematically describe the progressive development during heating. The upper side of the cube is Al–0.5%Mg alloy and its surface has been polished (under dry conditions). An oxide film grew on this polished surface during heating (see Fig. 10(b)). This thermally formed aluminum oxide film also generates micro-cracks during heating. Magnesium added in the Al alloy decreases its surface tension so that when the Al–0.5%Mg melts, the Al[Mg] melt can penetrate slightly into the gates of the micro-cracks. Magnesium possesses a higher vapor pressure than does aluminum, so that when heated and/or melted, magnesium could enter the micro-cracks channels first to carry out reaction (1); see appendix I. Again, oxygen originated from the surface layer of the deposited thermal oxide film/BM. MgO that formed at the gates or in the micro-cracks tended to react with Al\(_2\)O\(_3\) to form MgAl\(_2\)O\(_4\), \( (\Delta G_{1273K} = -26.5 \text{kJ/mol})\),\(^\text{15}\) leaving behind Al, see reaction (1). The micro-cracks might be sealed then reopened leading to the persistence of reaction (1) in the thermally formed aluminum oxide film.
The above process persisted. The reacted product, MgAl₂O₄, moved downward and accumulated at the diffusing channels (micro-cracks) in contact with the pure Al melt on the lower side. Before the residual thermal-formed oxide film fractured, the MgO and Al–Mg melt left behind the reacted MgAl₂O₄ layer, as shown in Fig. 10(d). When this layer increased in thickness to some extent, it then fractured, possibly due to thermal stress existed in the oxide film due to the generation of a great latent heat by the formation of MgO (Mg + 1/2O₂ → MgO, ΔH_{1000K} = −609 kJ/mol). The arrow in Fig. 9(a) points out one potential site for the fracturing of the MgAl₂O₄ layer.

3.4 A356.2 reacting with BM/oxide film

Both Mg and Si are necessary for growing alumina from liquid aluminum alloys. Yang explained that Si is more influential than Mg in the kinetics of forming alumina. The A356.2 used in this study contained 7.01%Si, and 0.34%Mg. A thin thermal oxide film formed on the polished surface of an A356.2 cube (up-side) during heating. This BM possessed a thermally formed aluminum oxide film.

For the sandwich experiment, when the heating time was short (720 s), we found that reaction (2) was prevalent in the diffusion channels (micro-cracks), due to the high concentration of silicon in the melt. The alumina oxide film was still compact and sound, as can be seen in the oxygen mapping in Fig. 11(a). When the heating time was extended to 780 s, the alumina oxide film became significantly decomposed along with the silica or silicon which had resided in the thermally formed aluminum oxide film, as shown in the oxygen
mapping in Fig. 11(b). Meanwhile, the A356.2 melt further penetrated into the oxide film via diffusion channels leading to an obvious increase in film thickness. The upper side of the melt brought some amounts of magnesium into the diffusion channels, which accelerated the oxide growth. Reaction (2) persisted at the diffusing channels leaving silicon or silica products within the film. The penetration at the melt also introduced Mg into the channels, leading reaction (1) to proceed locally. This significantly increased the thickness of the oxide film, as shown in Fig. 11(b).

When the heating time reached 900 s, the alumina oxide film decomposed and fractured. Figure 12(a) indicates although the oxide film might fracture it was still located in the central area of the sample. Silicon came from the upper melt to diffuse into the thermally formed aluminium oxide film via reaction (2). Consequently, the oxide film decomposed into a thin string, as shown by the oxygen mapping in Fig. 12(c). It is assumed that when an alumina oxide film (Al₂O₃) coexists with Mg and Si, it forms pyrope (ΔG₁₅₀₀K = −75 KJ/mol), and with Mg it forms spinel. Apparently, the whole oxide film string is composed of different oxides: pyrope and spinel along with some amounts of alumina, as shown in Fig. 12(f) (clarified by different colors). Notice the bottom part of Fig. 12(f), where silicon has diffused through the boundaries of different oxides to the lower melt or reacted with the spinel to form pyrope. Appendix II indicates that the structure of spinel is much more compact than pyrope. Silicon might diffuse through the boundaries of different oxides or through pyrope to the lower melt. The spinel is in contact with alumina, which indicates that the spinel originated from alumina, forming the reacted product from reaction (1).

4. Summary

A thermal oxide film was deposited on a pure aluminium surface. It contained micro-pore channels. When samples with this thermally formed oxide film were heated to 1023 K, and held for a period of time, micro-cracks in this thermally formed aluminium oxide film were initiated at the micropores. These micro-cracks coalesced to form cracks which drove gas bubbles to float upward. The induced upward stream in the pure Al melt fractured the oxide film.

When the pure aluminium oxide film sample was placed in contact with an Al–XSi cube and heated to 1023 K, the Al–XSi melt penetrated into the thermal oxide film through the micro-crack diffusion channels. The following reaction: 3[Si] + 3(O₂)−3[SiO₂] + 4[Al]−3[Si] + 2[Al₂O₃] occurred at the channels. The oxide film increased in thickness and was then gradually decomposed by the penetrating melt. When a sample of pure aluminium oxide film was placed in contact with an Al–Mg alloy and heated, MgAl₂O₄ gradually built up in the diffusion channels, increasing the thickness of the oxide film. Finally, the reacting MgAl₂O₄ fractured in the melt. When the sample with a pure aluminium oxide film was placed in contact with an A356.2 alloy and heated, the thermal oxide film decomposed first, via the following reaction: 3[Si] + 3(O₂)−3[SiO₂] + 4[Al]−3[Si] + 2[Al₂O₃]. It then gradually increased thickness and formed MgAl₂O₄. This product reacted with silicon or silica to form pyrope. The thermally formed oxide film was subsequently decomposed into different oxides and fractured in the melt.

5. Conclusion

The thermally formed alumina film formed crack during heating and became fractured when the gas escaped from the crack generating an upward moving stream in the pure Al melt. In the case of Al–Si melt, the alumina film significantly increased in thickness via reaction (2) at micropores and microcracks. The reactive products (silicon and/or silica) coexisted with alumina leading the thermal formed alumina gradually to decompose in the Al–Si melt. In the case of the Al–Mg melt, the reactive MgAl₂O₄ product formed, to build up at the interface of the penetrating Al–Mg melt and pure Al. This then fractured by the thermal stress. At the beginning of reaction the thermally formed alumina oxide film in the A356 melt was significantly affected by Si first and then formed MgAl₂O₄ and pyrope when the reaction time was extended. The reactive oxide film decomposed first and then fractured by the thermal stress in the A356 melt.

Fig. 11 Oxygen mapping of reacted oxide film in the experiment of BM/oxide film in contact with A356.2 alloy, heating at 1023 K for (a) 720 s, (b) 780 s.
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REFERENCES

3) M. J. Dignam, W. R. Faucett and H. Bohni: J. Electrochem. Soc. 113
Appendix I

![Diagram](image)

Micro-crack initiated from pore channel (a) during heating before melted

Thin oxide (Al₂O₃) film
Crack formed from the coalesced micro-cracks (b) during heating after melted

Reaction (1) or (2) persistently occurred leading the Al[Si]₆ or Al[Mg]₆ melt into the micro-cracks (c) during heating after melted

Al₂O₃ or Al[Si]₆ or Al[Mg]₆ melt into the micro-cracks (d) during heating after melted

Appendix II

![Diagram](image)

Spinel (MgAl₂O₄)

Pyrope (Mg₃Al₂Si₃O₁₂)

Tortuous pore channel; Pore Size (~ 0.105 nm)

Pore Size (~ 0.2 nm)