Effect of Ca on the Behavior of Double Oxide Film Defects in Commercially Pure Aluminum Melt

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The change in the composition of oxide layers and the possibility of the formation of bonding between the two layers of a double oxide film defect when held in Al-0.01 and 0.05 wt pct Ca melt was investigated, and the thermodynamics of the transformations occurring in the Al-Ca-Al_2O_3 system was studied. The defect was modeled experimentally by maintaining two aluminum oxide layers in contact with one another in the liquid metal at 1023 K (750 °C) for times ranging from 5 seconds to 50 hours. Any changes in the composition and morphology of these layers were studied by scanning electron microscopy and energy-dispersive X-ray spectroscopy. The results showed that the initial Al_2O_3 layer started to transform to a mixture of calcium aluminates in both alloys when the Al bars were still in the solid state. This transformation caused the two oxide layers to bond with each other gradually after the bars melted. The degree of bonding, however, was not consistent between the repetitions of the experiments, which was attributed to the difference between the initial H content of the melt on different experimental days.

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I. INTRODUCTION

FORMATION of a double oxide film defect in reactive liquid alloys such as Al or Mg was first described by Campbell.[1] During the casting process, every time the surface of the liquid metal folds upon itself, two surface oxide films come into contact with each other on their unwetted sides and a volume of gas (presumably predominantly air) is trapped between them. This defect (*i.e.*, two oxide layers with the volume of air trapped between them) which leads to a crack in the solidified casting not only deteriorates the mechanical properties of the casting, but also could act as an initiation site for the formation of other defects such as hydrogen pores[2] and Fe-rich phases[3] before solidification.

Raiszadeh and Griffiths[4] demonstrated that when a double oxide film defect moved in the liquid metal, cracks were formed on its oxide layers. First oxygen and then nitrogen of the trapped atmosphere of the defect came into contact and react with the surrounding Al melt through these cracks to produce Al_2O_3 and AlN, respectively. Using a semi-empirical mathematical model,[5] they suggested that this process took a few seconds to 2 minutes, depending on the size of the oxide defect and the severity of the turbulence in the melt.

It is suggested[6] that, if the two layers of an oxide film defect bond with each other, the most deleterious characteristic of the defect (*i.e.*, its crack-like nature) is eliminated, and therefore, the mechanical properties of the produced casting should be dramatically enhanced. Aryafar *et al.*[7] showed that after O and N of the trapped atmosphere within a defect that was held in an A356 aluminum melt was consumed, the two oxide layers of the defect gradually bonded with each other during the transformation of Al_2O_3 to $MgAl_2O_4$ and then to MgO. The occurrence of such bonding (dubbed healing[1]) was later confirmed for other aluminum alloys such as commercially pure,[8] Al-Mg,[9,10] and Al-0.05 wt pct Sr.[11]

Najafzadeh and Raiszadeh[8,9] concluded that, for the two layers of an oxide defect to bond with each other, two criteria must be met (1) complete consumption of O and N within the defect by the reaction with the surrounding melt, and (2) occurrence of a transformation involving the rearrangement of atoms at the internal surfaces of the oxide layers. They also observed that the two oxide layers of a double oxide film defect began to bond together when maintained in commercial purity Al melt for 5 hours. They attributed the bonding of the oxide layers to the transformation of γ- to α-Al_2O_3. The extent of the bonding was gradually increased by holding time so that the oxide layers almost completely bonded with one another after 48 hours.

Nateghian *et al.*[11] reported that addition of 0.05 wt pct Sr to the commercial purity Al melt completely changed the behavior of double oxide film defects and the bonding between the two oxide layers started immediately after the defect was submerged into the melt.

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The Gibbs free energy of formation of CaO is considerably more negative than that of Al_2O_3 (1062 and -907 kJ mole^{-1}, respectively, for the reaction of one mole O_2 at 1000 K (727 °C)[12]) and Ca readily reduces alumina to form CaO in aluminum melt. In contrast to Al_2O_3, the Pilling–Bedworth ratio (the ratio of oxide density to metal density) of CaO is less than unity (1.28 and 0.68, respectively[12]), and thus, Al melts containing Ca cannot maintain a continuous protective Al_2O_3 skin, even when the melt is quiescent. Instead, it will be subjected to rapid and continuous oxidation, which leads to formation of greater quantities of oxides.[13] Great tendency of Ca for oxidation and the non-protective nature of the resulting oxide should have a significant influence on the mechanism of healing of double oxide film defects in Al melt described previously by this research team. Studying this effect was the main goal of the present work.

II. EXPERIMENTAL PROCEDURE

A. *Modeling a Double Oxide Film Defect*

Aluminum alloys containing 0.01 and 0.05 wt pct Ca were prepared in a resistance-heated furnace by adding Al-10 wt pct Ca master alloy to a commercial purity Al alloy. Composition of the resulting alloys is shown in Table I.

The alloy was subsequently poured into silica sand molds with 5 pct sodium silicate and CO_2 gas as a binder in the shape of bars. The bars were machined to dimensions of 100 mm in length and 19 mm in diameter. Two bars were then placed in a seamless extruded steel tube (which was made specifically for gas industries) with dimensions of 210 mm in length and 20 mm in internal diameter. The bases of the bars that were in contact with one another in the steel tube were polished to 9 μm before the bars were inserted in the tube so that the naturally formed oxide layers resembled the two layers of a newly formed double oxide film defect.

The steel tube was then transferred to a cylindrical electric furnace with a sliding door at the top. The temperature of the furnace was set to 1023 K (750 °C) prior to the start of the experiment. The temperature of the Al bars increased at an average rate of 1.8 K s^{-1} (measured in a separate experiment using a K-type thermocouple inserted at the center of the steel tube), and the bars finally melted in the tube in 362 ± 1 second. The only possible leak path from the trapped atmosphere between the two oxide layers to the ambient atmosphere was through the gap between the oxide layer around the Al bars and the wall of the steel tube. To eliminate this leak path, the oxide layer around the top of the upper Al bar was removed with a sharp tool beneath the surface of the melt to remove the oxide separating the melt from the steel tube, ensuring direct contact between the melt and the tube. The Al bars were held in the liquid state for varying lengths of time, between 5 seconds and 50 hours, before the steel tube was raised in the furnace and held in the upper part of the heating chamber to let the liquid metal inside the tube solidify at a relatively slow rate (in approximately 40 seconds). Slow solidification of the metal was essential to prevent the formation of any thermal cracks on the two oxide layers inside the melt.

After solidification, the steel tube was cut into two halves and the Al bars were removed from it. In some experiments, the bonding formed between the two oxide layers during the experiment joined the two bars to each other. In this case, the two oxide layers were separated by pulling the two Al bars apart using a Zwick 1484 tensile testing machine at the strain rate of 1 mm min^{-1}. The surfaces of these two oxide layers were then examined using optical microscopy and a Camscan scanning electron microscope fitted with an Oxford Inca EDX for microanalysis.

Each experiment was repeated at least three times to confirm the repeatability of the results. More details of the experimental procedure can be found in another study by this research team.[7]

B. *Thermodynamic Study of Double Oxide Film Behavior*

Thermodynamics of the transformations that occurred in the Al-Ca-Al_2O_3 system and the possible reactions between the dissolved Ca in the Al melt and the alumina layers on the surface of the Al bars were studied using Equilib-Web, a part of the Fact-web program.[14] These calculations determined the amount of oxides present in the Al-Ca-Al_2O_3 system in the equilibrium state at 1000 K (727 °C) and 1 atm for Ca concentrations of 0.01 and 0.05 wt pct in the melt. In order to simplify the calculations, the Al_2O_3 layer was considered to be the only source of oxygen in the system and the variation in the thickness of this layer was considered to be equivalent to different amounts of oxygen in the trapped atmosphere (*i.e.*, different thicknesses of the trapped atmosphere).

III. RESULTS

A. *Al-0.05 Wt Pct Ca Alloy*

While the photographs of the oxide layers that were held in the furnace for 1 minute did not show any significant changes in the appearance of the layers, the SEM study of these layers revealed that some discon-

Table I. Composition of the Alloys Used in the Experiments

Alloy	Ca	Si	Cu	Pb	Fe	V	Al
Al-0.01 wt pct Ca	0.01	0.08	0.005	0.01	0.15	0.012	base
Al-0.05 wt pct Ca	0.05	0.1	0.01	0.01	0.1	0.013	base

tinuities were formed in them during this holding time. An example of such discontinuities is shown in Figure 1. The EDX analysis (see for example Figure 2) revealed that the concentration of Ca in these discontinuities was considerably higher than that of the melt. These figures revealed that the transformation of Al_2O_3 to a Ca-containing oxide started quite early, when the Al bars were still in the solid state with the temperature of about only 393 K (120 °C).

Figure 3 shows the photograph of the oxide layers that were held in the furnace for 4 minutes. It can be seen that a considerably large area of the oxide layers was altered. The bars, however, did not bond with each other and detached from one another after the experiment without requiring any force. Figure 4 illustrates an SEM micrograph from these layers. This figure shows that the discontinuities and the concentration of Ca in the oxide layers increased rapidly over time. Note that the Al bars were still solid at the holding time of 4 minutes.

From the holding time of 6 minutes, *i.e.*, when the Al bars melted in the steel tube, the bars partially bonded with each other and the bonding increased as the holding time increased. Strength of the bonding, however, was weak, and the bars were easily detached from each other by hand. Figures 5 and 6 which show the photograph and the SEM micrographs of the oxide layers that were held in the furnace for 20 minutes demonstrated that the bars bonded with each other in some areas and then the bonded areas were peeled off from the oxide layers during the separation of the Al bars.

The concentration of Ca in the oxide layer gradually increased over time. This change in the concentration of Ca in the oxide layer is evident in Figure 7, which shows the change in the average Ca/O ratio in the oxide layer measured by EDX as well as the concentration of Ca in the melt which was measured by mass spectroscopy from the solidified samples. The concentration of this element, however, decreased slightly after the holding time of 60 minutes.

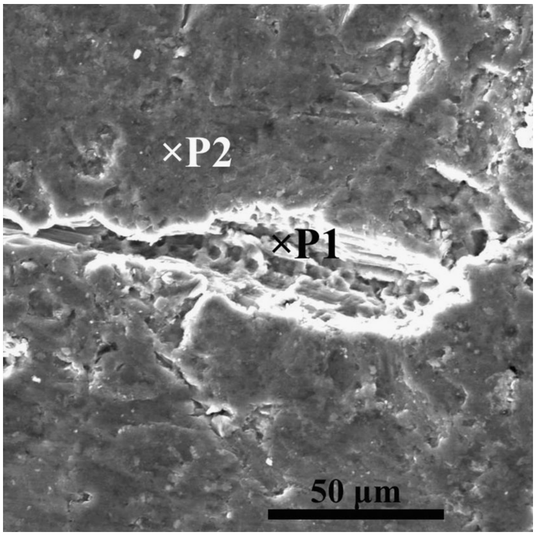

Fig. 1—SEM micrograph of the oxide layer in the Al-0.05 wt pct Ca experiment, after the bars were held in the furnace for 1 min. The EDS spectrum obtained from points P1 and P2 are shown in Fig. 2.

Figure 8 represents the photograph of the oxide layers that were held in the furnace for 60 minutes. It is evident in this figure that the two Al bars bonded with each other almost completely at this holding time. Such extensive bonding, however, was not observed in all the

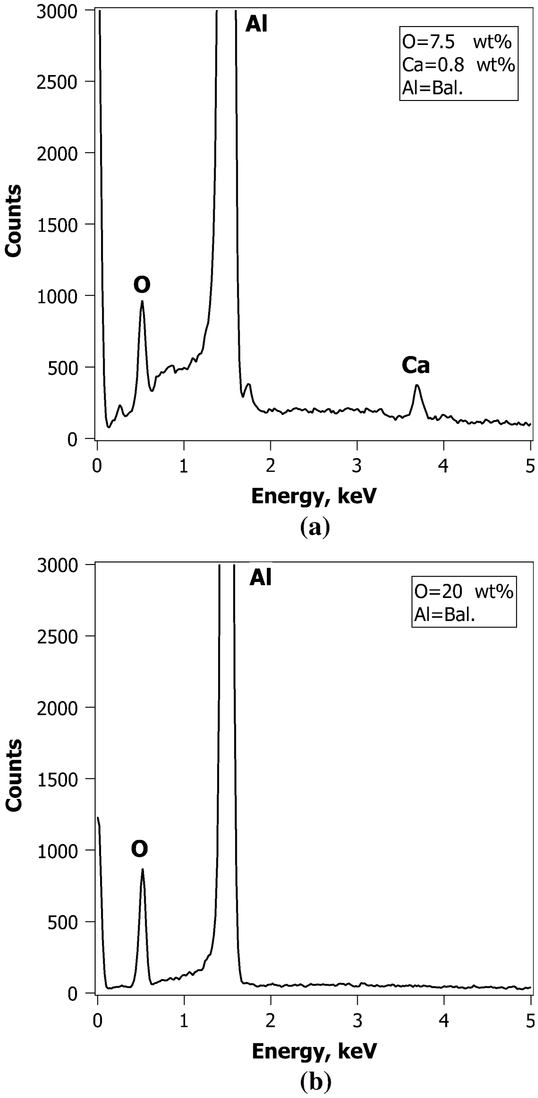

Fig. 2—EDS spectra obtained from points P1 and P2 in Fig. 1.

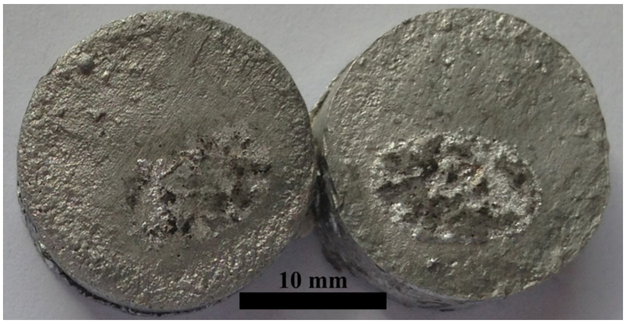

Fig. 3—Photograph of the oxide layers in the Al-0.05 wt pct Ca experiment held in the furnace for 4 min.

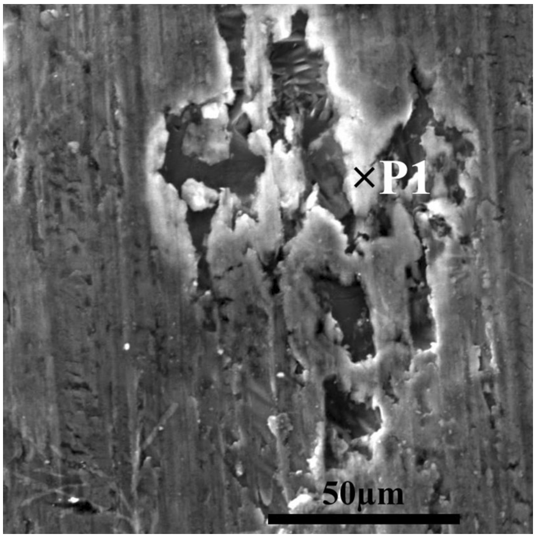

Fig. 4—SEM micrograph of the oxide layer in the Al-0.05 wt pct Ca experiment after the bars were held in the furnace for 4 min. The concentration of the elements at point P1 (all in wt pct) are O = 34 pct, Ca = 4 pct, and Al = Bal.

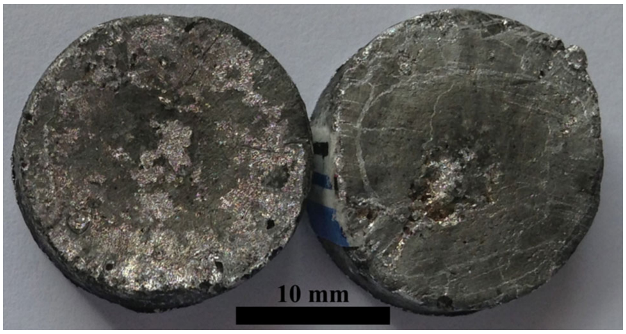

Fig. 5—Photograph of the oxide layers in the Al-0.05 wt pct Ca experiment held in the furnace for 20 min.

samples that were held in the liquid state for at least 60 minutes. An example of such a sample can be seen in Figure 9, which shows the photograph of the oxide layers that were held in the furnace for 180 minutes. Despite the relatively long holding time and the occurrence of the transformations in the oxide layers (which caused the layers to turn dark), the oxide layers bonded with each other only in a finite central area. The layers also did not seem to be flat and several ups and downs were visible on them.

B. *Al-0.01 Wt Pct Ca Alloy*

The very first change in the SEM micrograph of the oxide layers in the experiment with the Al-0.01 wt pct Ca alloy was observed when the Al bars were maintained in the furnace for 4 minutes, *i.e.*, 2 minutes before the bars melted in the steel tube. The Al bars started to bond with each other immediately after the bars melted at the holding time of 6 minutes. Figures 10 and 11 show the photograph and the SEM micrograph of the oxide layers at this holding time, respectively. Figure 11 demonstrates that a portion of the oxide layer which bonded with the opposite layer was peeled off from this layer when the bars were separated from each other. Bonding increased over time and the bars bonded with each other almost completely at the holding time of 150 minutes (see Figure 12(c)). Similar to the Al-0.05 wt pct Ca alloy, the severity of the bonding between the two layers in this alloy was also very variable among the repetitions of the experiment, as given in Figure 12. It is notable in this figure that, as the unevenness of the oxide layers increased, the bonding between the layers decreased.

The trend in the change of Ca/O ratio in this alloy was the same as that of the alloy containing 0.05 wt pct Ca. The concentration of Ca in the oxide layers increased first up to the holding time of 60 minutes and slightly decreased afterwards (see Figure 7).

C. *Results of Thermodynamic Calculations*

The thermodynamic calculations showed that the change in the thickness of double oxide film defect could affect the equilibrium phases in Al-Ca-Al_2O_3 system. In practice, this thickness is not constant and may vary with the amount of entrapped air between the layers of double oxide film defects. Therefore, the amount of entrapped air affects the composition of double oxide film and hence the nature of this defect. Figure 13 shows the stable phases in the Al-0.01 pctCa-Al_2O_3 system *vs* the thickness of double oxide film defect, calculated at 1023 K (750 °C) and 1 atm. This figure demonstrates that the Ca content of the alloy was not enough to form a pure CaO oxide and the stable phases were mixed oxides of $CaAl_2O_4$, $CaAl_4O_7$, and $CaAl_{12}O_{19}$ (briefly called CA, CA2, and CA6 in this paper). Ca content of these oxides decreased as the thickness of the oxide defect increased.

The Ca content of the alloy was not enough to form a pure CaO oxide even in the Al-0.05 wt pct Ca alloy (see Figure 14). Compared to the Al-0.01 wt pct Ca, however, the thickness of the oxide film defect for which any mixed oxides was stable considerably increased to about four to five-folds.

IV. DISCUSSION

Based on the standard Gibbs free energy data,[12] the oxidation of Ca is significantly more favorable than Al. Therefore, the chemical equilibrium path in the system Al-Ca-Al_2O_3 is toward the complete reduction of alumina by Ca to form CaO. However, when the amount of oxygen and/or calcium in the system is limited, the transformation cannot reach to its equilibrium state and different calcium aluminates might form as stable phases instead.

Dissolved Ca atoms in the liquid Al move toward the internal surface of the Al_2O_3 layer and begin to reduce it. The following reactions are possible between Ca and alumina.[14]

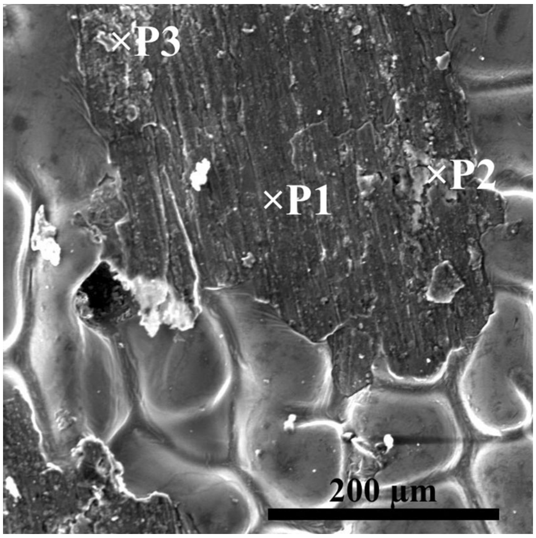

Fig. 6—SEM micrograph of the oxide layer in the Al-0.05 wt pct Ca experiment after the bars were held in the furnace for 20 min. (P1: O = 17, Ca = 4.5; P2: O = 39, Ca = 18; and P3: O = 31, Ca = 48; all in wt percent and Al = Bal.).

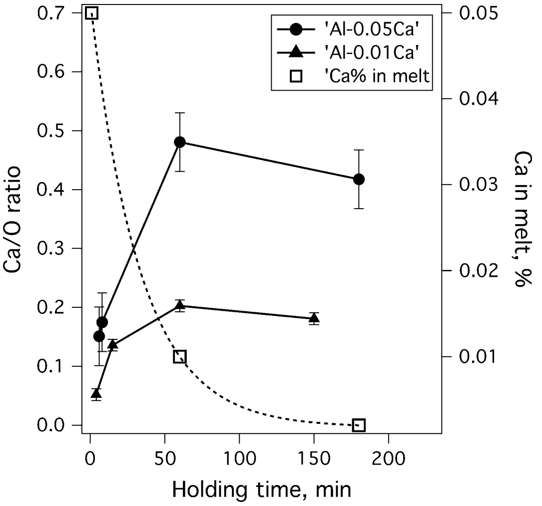

Fig. 7—Average Ca/Al ratio in the oxide layer and the concentration of Ca in the melt, measured by EDX and mass spectroscopy, respectively.

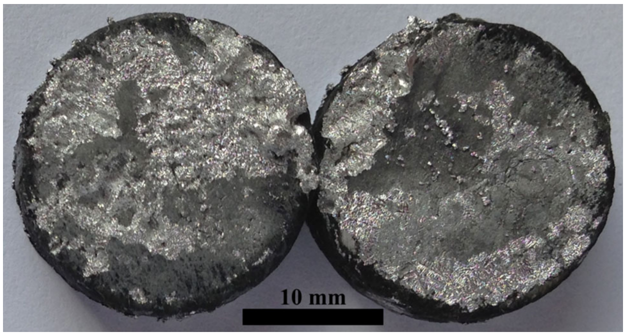

Fig. 8—Photograph of the oxide layers in the Al-0.05 wt pct Ca experiment that were held in the furnace for 60 min, demonstrating an almost complete bonding.

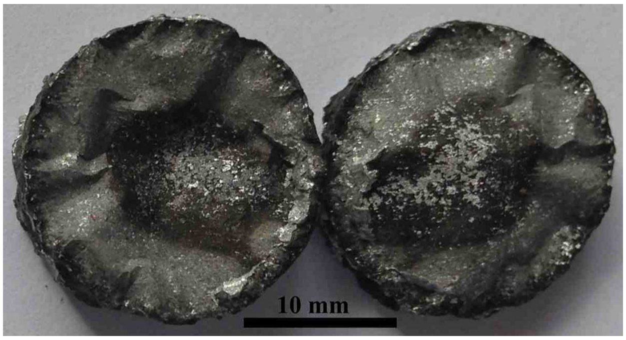

Fig. 9—Photograph of the oxide layers in the Al-0.05 wt pct Ca experiment that were held in the furnace for 60 min, demonstrating a finite bonding only in the central area.

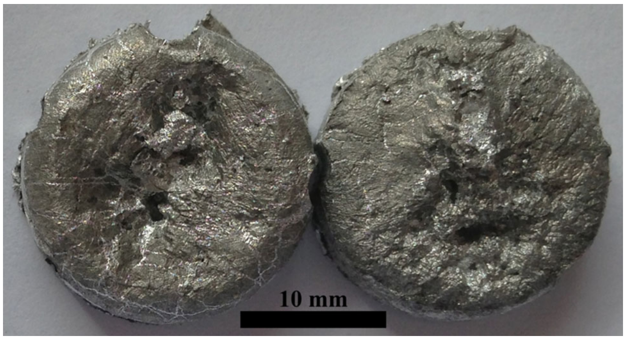

Fig. 10—Photograph of the oxide layers in the Al-0.01 wt pct Ca experiment that were held in the furnace for 6 min.

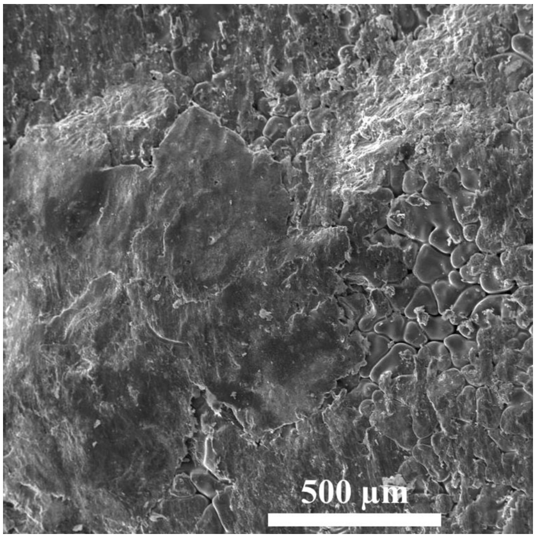

Fig. 11—SEM micrograph of the oxide layer in the Al-0.01 wt pct Ca experiment after the bars were held in the furnace for 6 min.

(a) **(b)** **(c)**

Fig. 12—Photograph of the oxide layers in the Al-0.01 wt pct Ca experiment that were held in the furnace for 150 min, showing a variable degree of bonding: (*a*) no bonding was formed, (*b*) bonding was formed in limited discreet areas, and (*c*) almost complete bonding was formed between the layers.

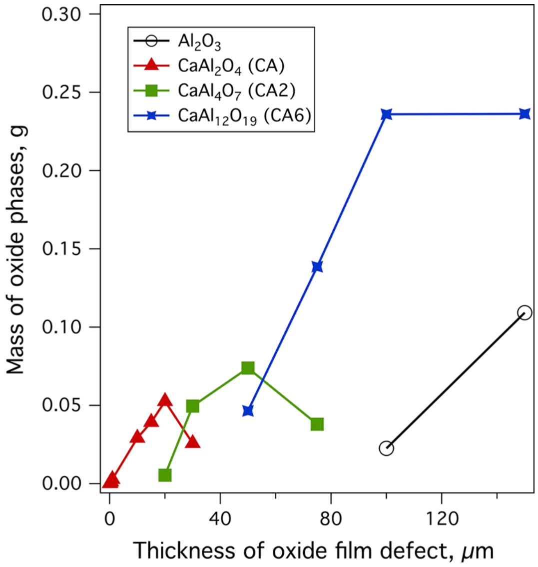

Fig. 13—Stable phases in the Al-0.01 pctCa-Al_2O_3 system *vs* the thickness of double oxide film defect calculated at 1023 K (750 °C) and 1 atm.

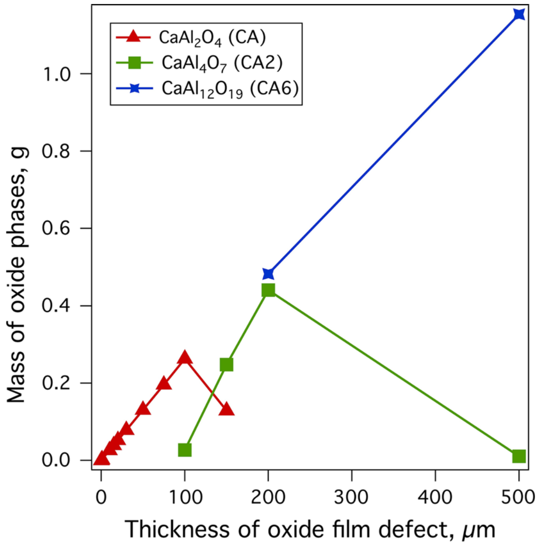

Fig. 14—Stable phases in the Al-0.05 pctCa-Al_2O_3 system *vs* the thickness of double oxide film defect calculated at 1023 K (750 °C) and 1 atm.

$$\mathrm{Ca(s)} + 19/3\ \mathrm{Al_2O_3(s)} = \mathrm{CaO.6Al_2O_3} + 2/3\ \mathrm{Al(l)} \qquad \Delta G_1 = -133.4831\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{Ca(s)} + 7/3\mathrm{Al_2O_3(s)} = \mathrm{CaO} \cdot 2\mathrm{Al_2O_3} + 2/3\mathrm{Al(l)} \qquad \Delta G_2 = -127.8798\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{Ca(s)} + 4/3\mathrm{Al_2O_3(s)} = \mathrm{CaO} \cdot \mathrm{Al_2O_3} + 2/3\mathrm{Al(l)} \qquad \Delta G_3 = -115.5959\ \mathrm{kJ\ mol^{-1}}$$

The products of these reactions are calcium aluminate phases resulted from partial reduction of alumina layer by Ca. These phases in brief are CA6, CA2, and CA, respectively. Based on Gibbs free energy values, the formation of CA6 phase is more favorable than CA2, and CA2 more favorable than CA. However, all of above reactions are thermodynamically possible and the products are stable.

The thermodynamic calculations (Figures 13 and 14) suggested that the type of calcium aluminate formed in the experiments was determined by at least two factors: the Ca content of the melt, and the thickness of the alumina layer. The increase in the Ca content of the melt led to the formation of calcium aluminate phases which were richer in Ca, such as CA rather than CA2 or CA6. On the other hand, the alumina layer, which provided oxygen for the reactions, had a great influence on the determination of the type of calcium aluminate phase formed.

The change in the Ca/O ratio observed in Figure 7 illustrated that Ca in both Al alloys with 0.01 and 0.05 wt pct Ca reduced the Al oxide layer to form a mixed oxide of Al and Ca. The rate of the reduction, however, decreased over time, which was probably due to the depletion of Ca in the molten alloy.

A simple calculation for the ratio of Ca/O in stable calcium aluminate phases gave 0.13, 0.35, and 0.63 for $CaAl_{12}O_{19}$ (CA6), $CaAl_4O_7$ (CA2), and $CaAl_2O_4$ (CA), respectively. The Ca/O ratio in the oxide layers reached the maximum of about 0.2 and 0.5 for the alloy containing 0.01 and 0.05 wt pct Ca, respectively (see Figure 7). Comparison of these values suggested that, in the alloy containing 0.01 wt pct Ca, the initial Al_2O_3 layer was transformed to CA6 in short times of <15 minutes, and then to a mixture of CA6 and CA2 in longer times of up to 60 minutes. During this time, the Ca content of the melt decreased dramatically from 0.05 to about 0.01 wt pct. Depletion of this element hindered the further progress of the transformation toward the formation of Ca-rich oxides.

A similar phase prediction was also possible for the alloy containing 0.05 wt pct Ca. According to Figure 7, the initial alumina layer was transformed to a mixture of CA6 and CA2 in short times of <15 minutes, and then to a mixture of CA2 and CA in longer times of up to 60 minutes. In both cases mixed oxide phases at longer experiment times seemed to be more stable and closer to equilibrium phases. Therefore, the oxide phases of Al-0.01 pct Ca and Al-0.05 pct Ca approached CA2 and CA phases, respectively.

The Ca/O ratio in the oxide layers decreased after the holding time of 60 minutes. Considering the very low concentration of Ca in the melt after this holding time, it can be speculated that this decrease was caused by further oxidation of aluminum melt by the oxygen that might be left in the trapped atmosphere through the cracks and other discontinuities present in the layers. The alumina that would be formed in this way would mix with the calcium aluminates already present in the layers and hence would decrease the concentration of Ca in the layer.

The tendency of Ca for reducing the alumina layer was so great that the transformation in the oxide layers started before the bars melted in the steel tube in both the Al alloys containing 0.01 and 0.05 wt pct Ca (see Figures 1 and 4). According to Aryafar *et al.*,[7] the occurrence of such transformation is essential for the two oxide layers to bond with each other. Another criterion for a successful bonding is the absence of air or hydrogen in the trapped atmosphere of the defect. Shafaei and Raiszadeh[15] demonstrated the importance of the timing of the occurrence of the transformations in the oxide layers on the efficiency of the bonding. If the transformations take a long time to occur, the bonding (healing) of the defect would be delayed accordingly and, if the transformations occur too quickly (or too early), before the gases in the trapped atmosphere have the chance to be consumed or diffuse back to the melt, then the bonding would not occur.

The results obtained in this work illustrated that the efficiency of the bonding between the two layers of the oxide films was significantly variable among the repetitions of the experiment (see Figure 12 as an example). Such variability was not observed by this research team in other alloys, such as Al-Mg,[9,10] Al-Sr,[11], or commercial purity Al.[8]

The difference between the initial H content of the melt on different experimental days (due to the difference in the humidity of the ambient atmosphere) could offer an explanation for this observation. Ca is known to increase the rate of oxidation of Al melt significantly,[16] and the oxidation of Al melt by the ambient moisture increases the H content of the melt. Dissolved hydrogen in the melt diffuses into the trapped atmosphere of the oxide defect and keeps the oxide layers separate from each other,[4] and hence prevents them from bonding. Aryafar *et al.*[7] observed that the bonding between the two layers of an oxide defect in Al-0.3 wt pct Mg occurred only after the H was diffused back to the ambient liquid Al (when the H content of the melt decreased due to equilibrating with the surrounding atmosphere). This reverse diffusion of H could take tens of minutes,[4] when, in the case of Al-Ca melts, it is too late for any bonding to occur, since the main part of the transformation in the oxide layers has occurred before this time. The surface of the oxide layers that did not bond with each other efficiently was observed to be uneven (see Figures 9 and 12), and this observation provided some evidence for this hypothesis.

V. CONCLUSIONS

1. The transformation of Al_2O_3 to a Ca-containing oxide in both Al-0.01 and 0.05 wt pct Ca melts started quite early, when the Al bars were still in the solid state.
2. The stable phases were predicted by the thermodynamic calculations as the mixed oxides of $CaAl_2O_4$ (CA), $CaAl_4O_7$ (CA2), and $CaAl_{12}O_{19}$ (CA6).
3. Comparison of thermodynamic calculations with the EDX studies suggested that the initial Al_2O_3 layer in the Al-0.01 wt pct Ca melt was transformed to CA6 in short times of <15 minutes, and then to a mixture of CA6 and CA2 in longer times of up to 60 minutes. In the Al-0.05 wt pct Ca melt, the initial alumina layer was transformed to a mixture of CA6 and CA2 in short times of <15 minutes, and then to a mixture of CA2 and CA in longer times of up to 60 minutes.
4. In both alloys, these transformations caused the two oxide layers to bond with each other in short holding times at a few points immediately after the bars were melted. The bonding increased gradually, as the transformation in the oxide layer progressed.
5. Degree of bonding, however, was not consistence between the repetitions of the experiments, which was attributed to the difference between the initial H content of the melt on different experimental days due to the difference in the humidity of the ambient atmosphere.

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