Probing the Initial Stage of Synthesis of Al_2O_3/Al Composites by Directed Oxidation of Al-Mg Alloys

H. VENUGOPALAN, K. TANKALA and T. DEBROY

In the directed oxidation of Al-Mg alloys, the amount of MgO that forms in the initial stage prior to the incubation period affects the rate of oxidation of Al to Al_2O_3 in the composite growth stage. The mechanism of formation of MgO and the duration of the initial stage were investigated experimentally and theoretically. The variables studied were total pressure in the reaction chamber, partial pressure of oxygen, and the nature of the diluent gas which affects the diffusion coefficients of magnesium vapor and oxygen in the gas phase. The oxidation rate in the initial stage was proportional to both the oxygen partial pressure and the diffusivity of oxygen. The duration of the initial stage decreased with the increase in oxygen pressure. To understand the role of magnesium evaporation in the oxidation behavior of the alloy, the velocity, temperature, and concentration fields in the gas phase were simulated numerically. The calculated concentration profiles of magnesium vapor and oxygen as a function of time were consistent with the experimentally measured oxidation rates and confirm reaction-enhanced gaseous diffusion-limited vaporization of magnesium in the initial stage of oxidation of Al-Mg alloys. The region where the magnesium vapor is oxidized in the gas phase moved progressively closer to the alloy surface during the initial stage of oxidation. The end of the initial stage and the start of the incubation period corresponded to the arrival of the oxygen front close to the surface when the spinel formation occurred.

I. INTRODUCTION

IN most structural applications, the primary disadvantage of ceramics is their lack of toughness, which renders them sensitive to sudden failure in response to accidental overloading, contact damage, or rapid temperature cycling. This deficiency has led to attempts to produce ceramic matrix composites which provide adequate toughness and other desirable properties. The directed oxidation of molten aluminum alloys by vapor phase oxidants can be used to produce tough ceramic matrix composites. The composite formation process involves rapid reaction of the molten aluminum alloy with oxygen to form α-Al_2O_3.[1] The reaction is sustained by the wicking of liquid metal along interconnected microscopic channels in the reaction product.[1] The resulting material is an Al_2O_3/Al composite with a three-dimensional network of metal channels.[2] Reinforced composites are formed by growing this "composite matrix" into preforms consisting of reinforcing particulates or fibers of Al_2O_3 and SiC.

The directed oxidation of aluminum alloys depends crucially on certain alloying elements like magnesium and zinc.[1] Magnesium and zinc form oxides (MgO and ZnO) at the surface, which prevent the passivation of the melt and facilitate the continuous supply of oxygen to the reaction interface.[3,4] Figure 1 is a typical weight gain *vs* time curve observed during the oxidation of Al-Mg alloys at a given temperature. Three different stages can be distinguished. An initial stage of rapid weight gain, associated with the formation of MgO, terminates with the onset of incubation, which is a stage of very slow growth. This sharp decrease in rate is believed to occur due to the formation of a dense, thin (≈ 1 μm) layer of $MgAl_2O_4$ beneath the MgO.[5] At the end of incubation, there is an increase in the weight gain rate corresponding to the bulk oxidation of Al to Al_2O_3. Nagelberg *et al.*[6] postulated that the bulk oxidation of Al-Mg-Si alloys is controlled by the flux of oxygen through the external MgO layer and is inversely proportional to the thickness of the MgO layer. Furthermore, Xiao and Derby[7] have shown that composite growth can be achieved with pure aluminum provided MgO powder is placed on top of the aluminum. They[7] also observed that the growth rate increased with the increase in the amount of MgO. These results indicate the crucial role of MgO in the composite growth. Thus, the rate of formation of MgO, the duration of the initial stage of oxidation, and the amount of MgO formed in the initial stage are important.

Formation of MgO in the initial stage of oxidation has been observed by several investigators. The presence of MgO in the top crust of the oxidation product of Al-5083 alloy heated in air at 1217 K for 3 hours was confirmed by X-ray diffraction in our recent work.[8] Vlach *et al.*[5] suggested that the formation of MgO in the initial stage of oxidation occurs by reaction-enhanced, gaseous-diffusion-limited vaporization of Mg followed by its oxidation. However, no experimental evidence was presented to corroborate the suggested mechanism. They[5] also suggested that the initial stage of oxidation ends when a dense layer of spinel forms on the surface of the melt and prevents further vaporization of magnesium. However, no explanation for the sudden formation of spinel, leading to the sharp decrease in the rate at the end of the initial stage of oxidation, was presented. Although the amount of MgO at the

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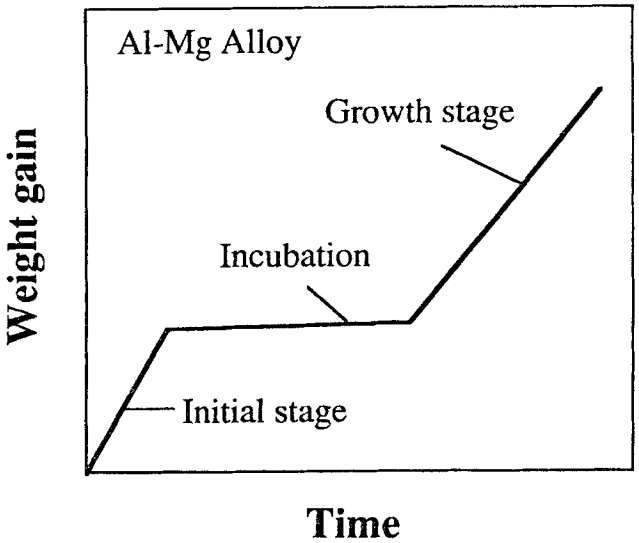

Fig. 1—Schematic plot of weight gain as a function of time for directed oxidation of Al-Mg alloys.

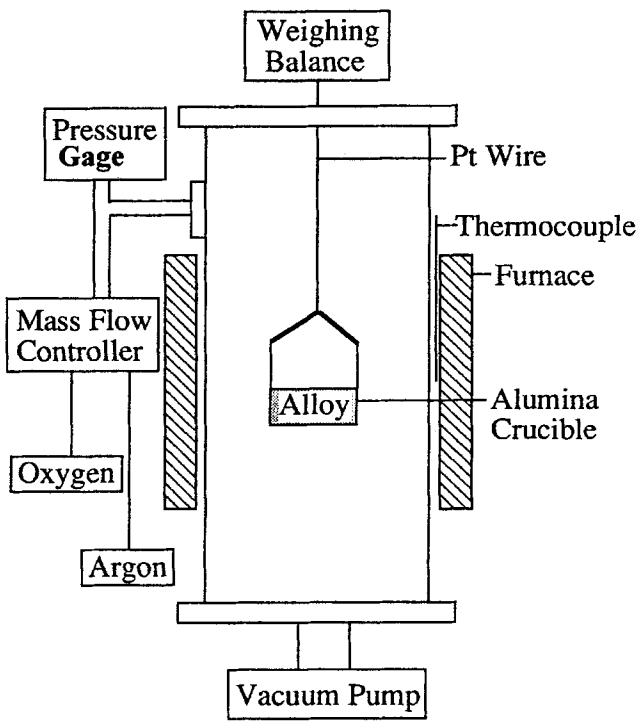

Fig. 2—Schematic diagram of the experimental setup.

surface of the melt plays an important role in the bulk oxidation of Al-Mg alloys, a review of the literature on directed oxidation of aluminum alloys reveals that the mechanism and the reason for the abrupt end of the initial stage of oxidation are not clearly understood.

The vapor pressure of magnesium is considerable over most Al-Mg alloys at temperatures commonly used in the directed oxidation process. Thus, the vaporization of magnesium and its subsequent vapor phase oxidation are important in the composite growth. Turkdogan *et al.*[9] and Wagner[10] proposed a model for the vaporization of pure metals in a reactive atmosphere. They showed that the rate of vaporization was independent of the vapor pressure of the metal but dependent on the partial pressure of the reactive gas. In their study, the vapor pressures of metals were significantly lower than the partial pressure of the reactive gas, oxygen. This is not the case in the directed oxidation of Al-Mg alloys, since the vapor pressure of Mg is comparable to the oxygen partial pressures typically used in the oxidation of the Al-Mg alloys. Furthermore, unlike the vapor pressure of a pure metal, the vapor pressure of magnesium over the Al-Mg alloy decreases continuously with time as vaporization proceeds, owing to the depletion of magnesium from the alloy. Thus, the reaction-enhanced vaporization of Mg into the gas phase must be coupled with the loss of magnesium from the alloy to accurately calculate the rate of Mg vaporization and, consequently, the rate of vapor-phase oxidation of magnesium in oxygen atmosphere in the initial stage of directed oxidation.

In this article, the rates of oxidation of Al-Mg alloys in the initial stage of oxidation and the duration of the initial stage are examined experimentally and theoretically. The weight gain rates and the duration of the initial stage are measured thermogravimetrically as a function of the oxygen partial pressure, nature of the diluent gas, and the total pressure in the system. In order to understand the role of magnesium evaporation in the initial oxidation behavior of the alloy, the diffusion coefficient of magnesium vapor is varied by changing the total pressure and the type of diluent gas. Numerically simulated velocity, temperature, and concentration profiles in the gas phase are used to explain vaporization of Al-Mg alloys in an oxidizing atmosphere. The model predictions of the extent of MgO formation in the initial stage of oxidation are in good agreement with the experimental results. Furthermore, it is shown that the end of the initial stage corresponds to the arrival of the oxygen front close to the surface of the melt when spinel formation occurs.

II. PROCEDURES

The thermogravimetric setup, used for studying the kinetics of reaction in the directed oxidation of Al-Mg alloys, consisted of a Cahn model 1000 automatic recording electric balance, a high-temperature silicon carbide tube furnace, and a gas flow and pressure control system. A schematic diagram of the experimental setup is shown in Figure 2. The balance had a sensitivity of 0.5 mg, and the measurement accuracy was 0.1 pct of the recorder range. The quartz reaction tube had a 48-mm i.d. and a 25-mm equitemperature zone at the center of the furnace. The furnace was equipped with an electronic temperature controller which regulated the temperature to ± 5 K.

A cylindrical sample, 14 mm in diameter and 8 mm in length, of an Al 5056 alloy (5 wt pct Mg, 0.10 wt pct Cu, 0.40 wt pct Fe, 0.10 wt pct Zn, 0.10 wt pct Mn, and balance Al) was placed in an alumina crucible, 14.2 mm in diameter and 27 mm in length. The crucible, containing the alloy, was suspended by a platinum wire from the balance and positioned within the equitemperature zone of the furnace. Prior to conducting each experiment, the reaction tube was evacuated and purged with argon. The samples were then heated to 1391 K, at a heating rate of 0.33 K/s, in a pure argon atmosphere. A weight loss of 1 to 5 mg is observed during initial heating in argon. The magnesium concentra-

tion in the alloy is corrected for this initial vaporization loss in the calculations. When the target temperature was reached, a mixture of ultrahigh-purity oxygen and inert gas, argon, or helium was introduced, and the flow rates of oxygen and inert gas were controlled with the help of mass flow controllers to obtain a predetermined gas composition. Oxidation experiments were conducted at various partial pressures of oxygen and reactor pressures. The total gas flow rate was kept constant at 3333 mm^3/s STP (298 K and 10,130 Pa). Experiments were repeated to check the reproducibility of the weight gain data. A typical scatter of 1 to 5 pct was observed in the weight gain measured during the initial oxidation. The weight gain *vs* time data were recorded on a strip chart recorder in each case. The nominal cross-sectional area of the sample, 154 mm^2, was used for the calculation of reaction rates. The end of the initial rapid weight gain stage was considered to be the time when there was a sharp drop in the weight gain rate.

The velocity, temperature, and concentration fields in the gas phase during the initial stage of oxidation were computed by solving equations of conservation of momentum, enthalpy, and concentration of magnesium vapor and oxygen, which are represented in the following form:

$$\frac{\partial}{\partial t}(\rho\phi) + \frac{\partial}{\partial x_i}(\rho u_i \phi) = \frac{\partial}{\partial x_i}\left(\Gamma \frac{\partial \phi}{\partial x_i}\right) + S \qquad [1]$$

where t is the time; ρ is the density; u_i is the component of velocity in the i direction; ϕ is the dependent variable which can represent velocity components, temperature, or concentration; S is the volumetric source term; and Γ is the diffusion coefficient which is given an appropriate meaning depending on the variable considered. The details of the specific equations in cylindrical coordinates are described in standard textbooks[11,12] and are not presented here. The calculations were performed for a two-dimensional, unsteady, laminar flow case considering spatial variation of density and diffusion coefficient. The equations of conservation of mass, momentum, and energy, represented by Eq. [1], were expressed in a finite difference form and solved iteratively on a line-by-line basis. The details of the solution procedure are described elsewhere.[12,13] A nonuniform grid spacing was used for obtaining maximum advantage in the resolution of variables. The calculations were done for the duration of the initial stage of oxidation.

The input to the model included the size and shape of the reactor and its contents, the physical properties, the rate of supply, and the composition of the input gas mixture and the heating conditions. The velocity, temperature, and concentration fields of magnesium vapor and oxygen were obtained from the calculations. The boundary conditions included prescription of the input parabolic velocity distribution at the top of the reactor based on the total gas flow rate. The temperature of the inlet gas stream was prescribed to be the room temperature. At the axis of the reactor, the velocity, temperature, Mg vapor, and oxygen concentration gradients were taken to be zero based on the symmetry consideration. At the reactor wall, the velocities were assumed to be zero on the basis of a no-slip condition, and the fluxes of magnesium vapor and oxygen were taken to be zero. At the reactor wall, a temperature of 1391 K was specified in the equitemperature zone, while a measured wall temperature profile was prescribed from the inlet to the equitemperature zone. At the melt surface, the vapor pressure of Mg is specified as the equilibrium vapor pressure over the alloy, the oxygen concentration is set to zero, the velocities are set to zero, and the temperature is specified. At the bottom outflow boundary, the velocity, temperature, and concentration fields were assumed to be fully developed.

At the start of the calculations, the equilibrium vapor pressure of magnesium at the melt surface was determined from the initial alloy composition, temperature, and activity coefficient of magnesium in the Al-Mg alloy.[14,15] Computation of the Mg concentration field in the liquid, for the observed vaporization rates, indicates that a sufficient amount of convection occurs to ensure homogenization of Mg in the liquid alloy. Therefore, the Mg concentration in the bulk of the Al-Mg alloy melt is taken to be the same as that at the surface. For this known concentration of magnesium vapor at the alloy surface, the concentration profiles of magnesium and oxygen in the gas phase were determined. The magnesium flux from the alloy melt into the gas phase and the corresponding weight loss from the Al-Mg melt were calculated from the magnesium vapor concentration profiles. At the next time-step, the vapor pressure of magnesium at the melt surface was updated based on the change in magnesium concentration in the alloy melt. Since the reaction of Mg vapor with oxygen to form MgO is rapid (Eq. [2]), it is assumed that magnesium vapor and oxygen cannot coexist in the gas phase.

$$\mathrm{Mg\ (g)} + \frac{1}{2}\mathrm{O_2\ (g)} = \mathrm{MgO\ (s)} \qquad [2]$$

If the ratio of the number of moles of magnesium in the gas phase to the number of moles of oxygen is greater than 2 during any iteration, the oxygen concentration is set to zero and *vice versa*. It is therefore valid to assume binary diffusion coefficients for each species in the reactive atmosphere. The MgO, formed by the vapor phase reaction of oxygen and Mg vapor, falls back onto the alloy melt surface and is registered as a gain in the weight of the crucible by the automatic recording balance.

III. RESULTS AND DISCUSSION

Figure 3 shows the weight gain of the Al-Mg alloy samples as a function of time for various oxygen partial pressures at a temperature of 1391 K and total pressure of 93,303 Pa. It is observed from the figure that both the total weight gain during the initial stage of oxidation and the duration of the initial stage decrease with increasing partial pressure of oxygen. Furthermore, the rate of oxidation increases with increasing oxygen pressure. In all cases, the initial stage of oxidation ends abruptly. In addition, a close examination of the data indicates that the weight gain rate decreases with time at low oxygen pressures and is constant at high oxygen pressures. Several interesting questions arise from a perusal of these data. What is the mechanism of initial stage oxidation of Al-Mg alloys? Why does the weight gain rate decrease with time at low oxygen pressures and why is the rate independent of time at high oxygen pressures? Why is the duration of the initial stage short at high oxygen pressures? Why does the initial stage end abruptly?

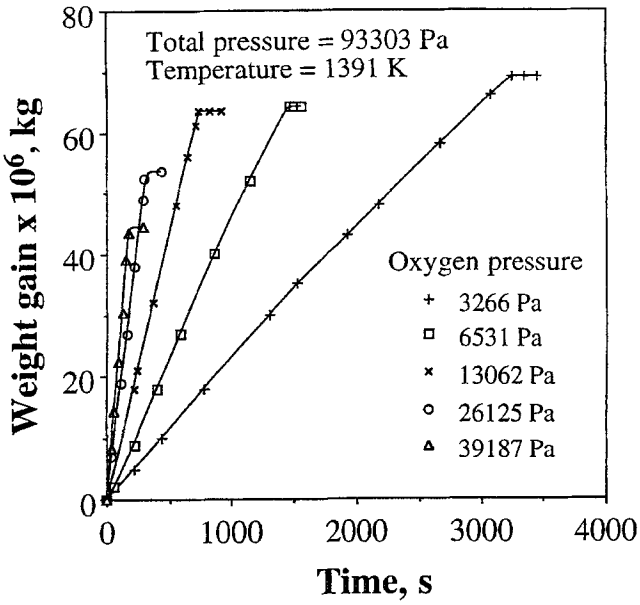

Fig. 3—Plot of weight gain *vs* time for various oxygen pressures.

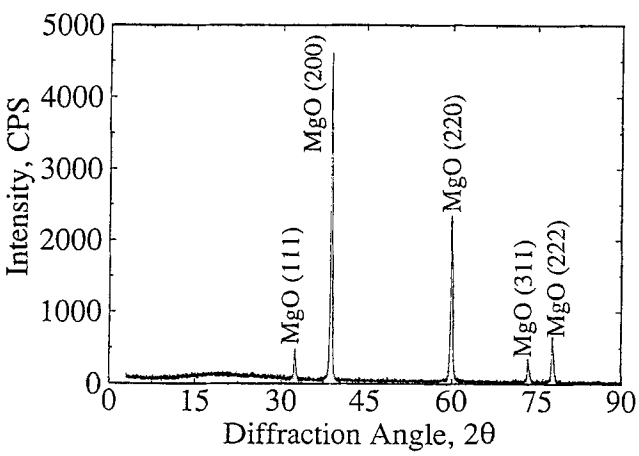

Fig. 4—X-ray diffraction pattern of the white powder formed on the crucible walls during the initial stage of oxidation of Al-Mg alloys.

The oxidation experiments were terminated at the end of the initial stage and the samples were examined. A loose, fine, white powder was observed on the surface of the sample and on the inner walls of the crucible. X-ray diffraction data of the white powder on the sample and on the walls of the crucible, presented in Figure 4, indicated the powder to be MgO. The presence of MgO on the walls of the crucible indicates that the mechanism of oxidation in the initial stage involves evaporation of magnesium from the melt followed by its oxidation in the vapor phase.

The velocity, temperature, and concentration fields of oxygen and magnesium in the gas phase were computed to understand the vapor phase oxidation of magnesium. Figure 5 shows the computed velocity field and the concentration profiles of magnesium and oxygen in the gas phase at the initiation of oxidation for an oxygen partial pressure of 3266 Pa, a total pressure of 93,303 Pa at 1391 K. The data used for the calculations are presented in Table I. The calculated velocity field indicates that the velocity of the gas is negligible within the crucible above the melt surface because the gas is confined in this region. The computed concentration field, presented in Figure 5, shows that the concentration profiles within the crucible are parallel to the melt surface, indicating that the profiles are established primarily by diffusion and are not influenced by convection. The relative importance of convection and diffusion within the crucible can be examined from the Peclet number for mass transfer, which is the ratio of convective mass transfer to diffusive mass transfer. The Peclet number for mass transfer, Pe, is given by Pe = uL/D, where u is the velocity, L is the characteristic length, and D is the diffusion coefficient. An order of magnitude calculation of Pe gives a value of 4.6×10^{-3}, indicating that mass transfer in the gas phase occurs primarily by diffusion. Thus, the concen-

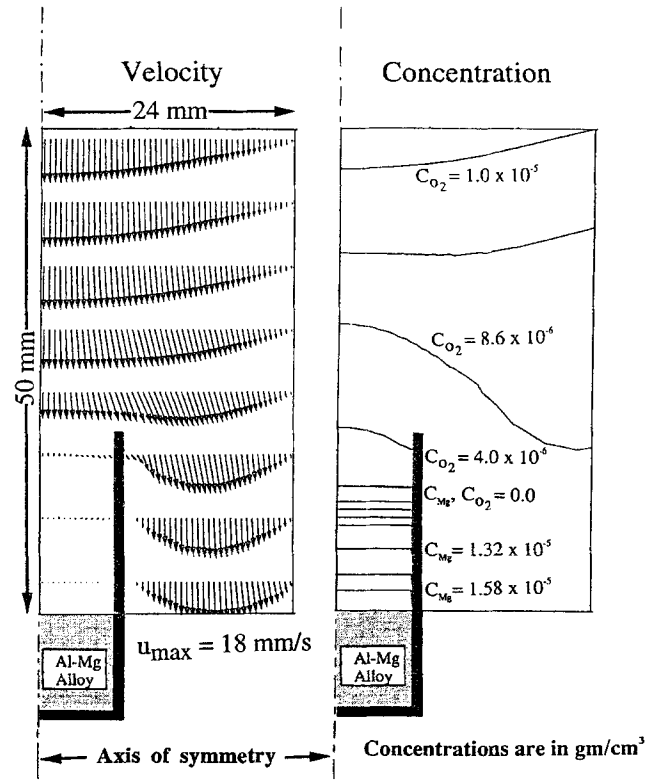

Fig. 5—Computed velocity and concentration profiles of magnesium and oxygen in the gas phase, for an oxygen pressure of 3266 Pa, and total pressure of 93,303 Pa at 1391 K, at the initiation of the experiment. (Note: 1 g/cm³ = 10³ kg/m³.)

Table I. Data Used for the Calculations

Property	Symbol	Value
Pressure	P	1.33×10^4 to 9.33×10^4 Pa
Thermal conductivity	k	4.14×10^{-2} J/(m s K)
Specific heat	C_P	520 J/(Kg K)
Viscosity	μ	4.78×10^{-5} kg/(m s)
Diffusion coefficient	$D_{O_2\text{-}Ar}$	3×10^{-4} (700/P) $(T/1391)^{1.5}$ m²/s
	$D_{Mg\text{-}Ar}$	3×10^{-4} (700/P) $(T/1391)^{1.5}$ m²/s
Density*	ρ	PM/(RT) kg/m³

*M is the molecular weight of the gas mixture.

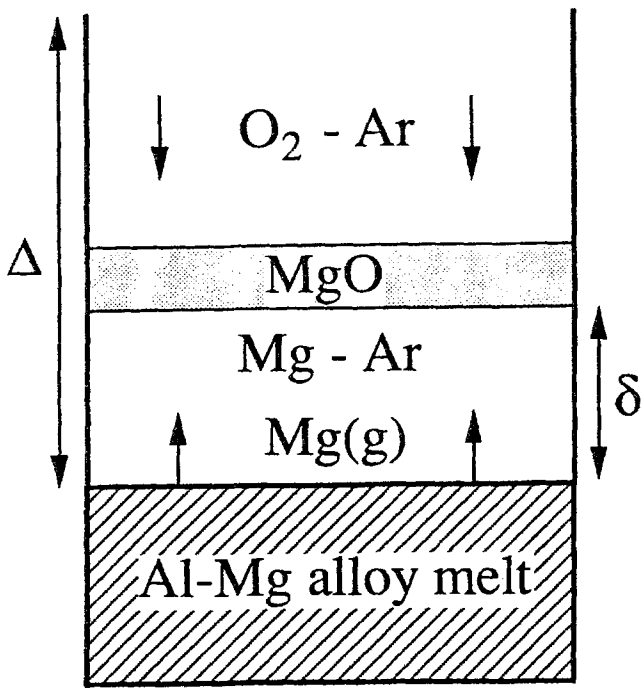

Fig. 6—Schematic diagram showing the magnesium and oxygen boundary layers formed in the gas phase above the melt and within the crucible during the initial stage of oxidation of Al-Mg alloys.

tration profiles are consistent with the calculated Peclet number for mass transfer.

The velocity and concentration profiles, presented in Figure 5, indicate that a diffusion boundary layer is established within the crucible. A counter diffusion of Mg-vapor and O_2 gas in argon takes place. At a short distance from the surface of the alloy, Mg vapor reacts with oxygen, forming an MgO mist according to Reaction [2]. The concentration profile indicates that the reaction of Mg vapor and oxygen to form MgO in the gas phase occurs within the confines of the crucible. Hence, all the MgO formed by the vapor phase oxidation fell back onto the crucible and was registered as a weight gain by the balance. Since the formation of MgO requires 1 mole of oxygen for every 2 moles of Mg vapor, the Mg vaporization rate, calculated from the model, can be used to determine the corresponding weight gain rate and can be compared with the experimentally observed rate.

It is observed from Figure 5 that the gas phase is divided into two distinct zones, a magnesium vapor-argon region close to the melt surface and an oxygen-argon region above this region. A schematic diagram showing this division of the boundary layer and the formation of an MgO mist is presented in Figure 6. At any given instant, the molar fluxes of magnesium vapor, J_{Mg}, and oxygen, J_{O_2}, are given by

$$J_{Mg} = \frac{D_{Mg}\,(p_{Mg} - p^i_{Mg})}{\delta RT} \qquad [3]$$

$$J_{O_2} = \frac{D_{O_2}\,(p_{O_2} - p^i_{O_2})}{(\Delta - \delta)\,RT} \qquad [4]$$

where D_{Mg} is the interdiffusivity of the Mg (g)-Ar pair, D_{O_2} is the interdiffusivity of the Ar-O_2 pair, δ is the distance between the alloy surface and the location in the vapor phase where MgO forms. Δ is the sum of the thicknesses of Mg and O_2 boundary layers, T is the temperature, p_{Mg} is the vapor pressure of Mg at the surface of the alloy, p^i_{Mg} and $p^i_{O_2}$ are the partial pressure of magnesium and oxygen at the reaction interface, respectively, and p_{O_2} is the partial pressure of oxygen at a distance Δ from the surface of the alloy. Since p^i_{Mg} and $p^i_{O_2}$ are much smaller than p_{Mg} and p_{O_2}, respectively, they can be neglected in Eqs. [3] and [4]. From the stoichiometry of Reaction [2], we obtain

$$J_{Mg} = 2\,J_{O_2} = \frac{2D_{O_2}\,p_{O_2}}{(\Delta - \delta)\,RT} \qquad [5]$$

For nonzero values of p_{O_2} and p_{Mg}, we can rearrange Eqs. [3] through [5] to obtain

$$J_{Mg} = \frac{2\,D_{O_2}\,p_{O_2}}{RT\Delta}\left[1 + \frac{D_{Mg}\,p_{Mg}}{2\,D_{O_2}\,p_{O_2}}\right] \qquad [6]$$

and the weight gain rate, R, based on the stoichiometry of the reaction is given by

$$R = 0.5\,M_{O_2}\,J_{Mg} = \frac{M_{O_2}\,D_{O_2}\,p_{O_2}}{RT\Delta}\left[1 + \frac{D_{Mg}\,p_{Mg}}{2\,D_{O_2}\,p_{O_2}}\right] \qquad [7]$$

Furthermore, since $D_{Mg} \approx D_{O_2}$, we have

$$R = 0.5\,M_{O_2}\,J_{Mg} = \frac{M_{O_2}\,D_{O_2}\,p_{O_2}}{RT\Delta}\left[1 + \frac{p_{Mg}}{2\,p_{O_2}}\right] \qquad [8]$$

The vapor pressure of Mg over the melt for the starting alloy composition of 5 wt pct Mg is 5838 Pa. It is seen from Eq. [8] that for an oxygen pressure of 3266 Pa, the second term within the bracket is of comparable magnitude to the first term, which is one. Therefore, both terms within the bracket have an equal influence on the weight gain rate. As Mg concentration in the melt decreases with time due to vaporization, the Mg vapor pressure over the melt decreases, and hence, less oxygen is consumed in the reaction. Thus, p_{Mg} and, consequently, the weight gain rate change with time. Figure 7(a) shows a comparison of the experimental and calculated weight gain with time for an oxygen partial pressure of 3266 Pa. It is observed that the calculated weight gain is in good agreement with experimental data. Furthermore, the slope of the weight gain curve decreases with time, indicating a decrease in the weight gain rate from start to finish of the initial stage of oxidation. Thus, the model explains the decrease in weight gain rate with time at low oxygen partial pressures.

At an oxygen pressure of 39,187 Pa, the second term in Eq. [8] is of much smaller magnitude than the first term (which is one) within the bracket. Therefore, any decrease in the second term due to a decrease in Mg vapor pressure with time does not change the values of the terms within the square bracket significantly. At high oxygen pressures, the rate of reaction-enhanced vaporization of a volatile constituent of an alloy is mildly dependent on the vapor pressure of the constituent and strongly dependent on the oxygen partial pressure. This constant weight gain rate with time at high oxygen pressures is clearly seen in Figure 7(b) for an inlet oxygen pressure of 39,187 Pa, where the weight gain rate changes by 5 pct from the start to the end of the initial stage, while the Mg composition in the alloy changes from 5.5 to 2.93 mole pct. Thus, the model predictions are consistent with the observed trends in weight gain rate at both low and high oxygen pressures.

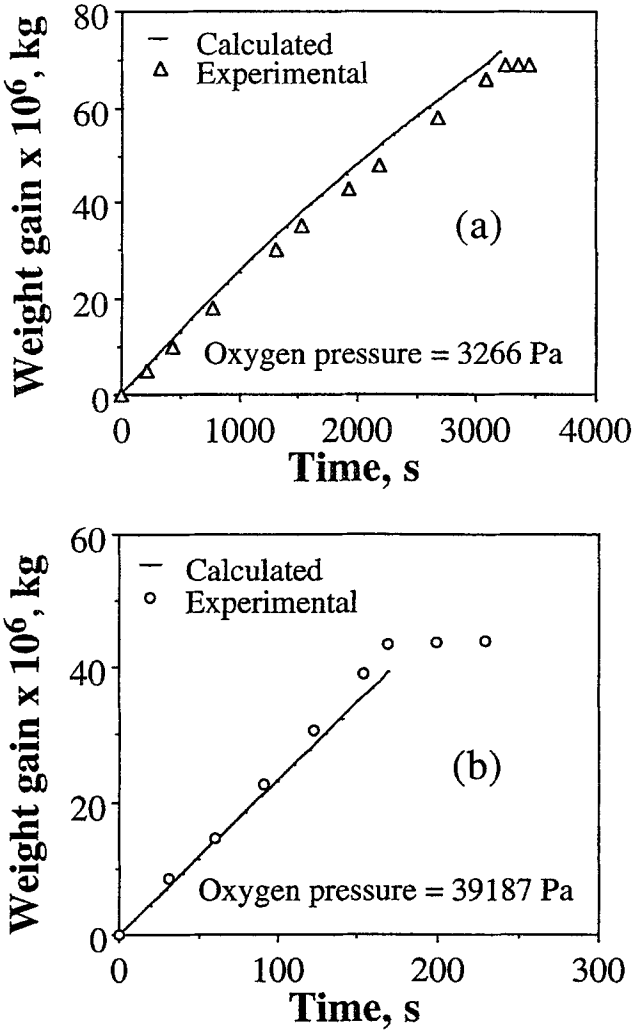

Fig. 7—Comparison of experimental and calculated weight gain *vs* time for oxygen pressures of (*a*) 3266 Pa and (*b*) 39,187 Pa. Experiments were done at 1391 K and 93,303 Pa total pressure.

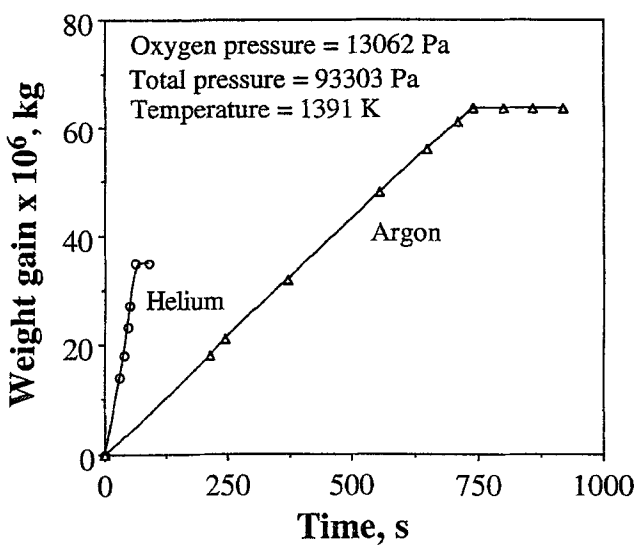

Fig. 8—Weight gain *vs* time during initial stage of oxidation of Al-Mg alloys in O_2-Ar and O_2-He atmospheres.

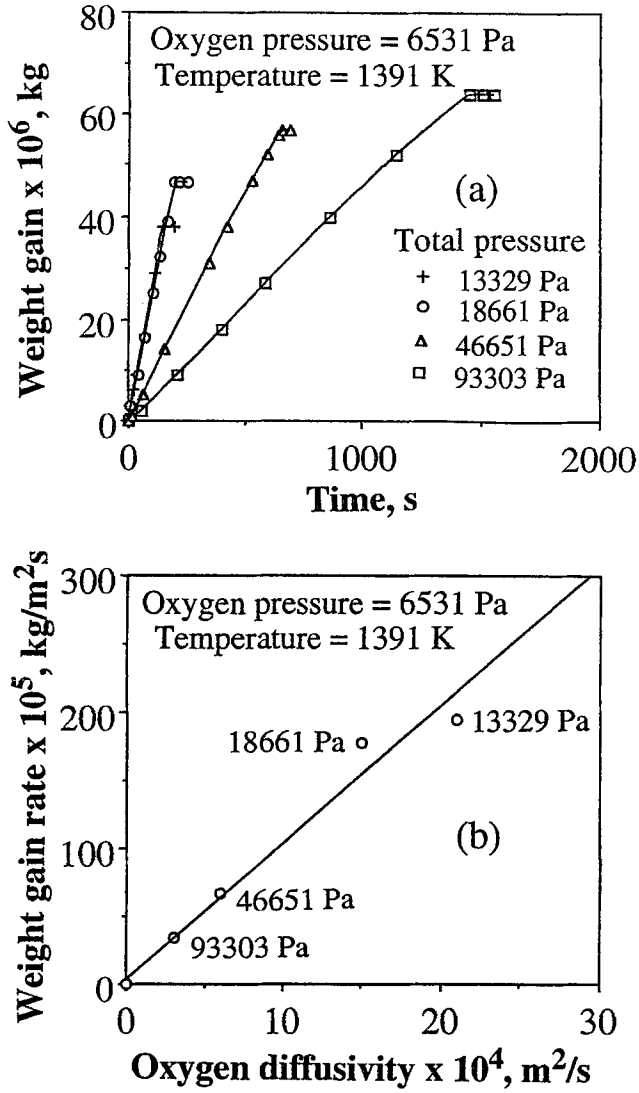

Fig. 9—(*a*) Weight gain *vs* time in the initial stage of oxidation for different total pressures. (*b*) Weight gain in the initial stage *vs* oxygen diffusivity in the reactive atmosphere.

Equation [8] indicates that the weight gain rate is influenced by the diffusivity of oxygen in the gas phase. If the vaporization of magnesium is diffusion limited, a change in diffusion coefficient would result in a corresponding change in the weight gain rate. Two sets of experiments were conducted to confirm the reaction-enhanced gaseous diffusion limited vaporization of magnesium. In one set, the oxidation was carried out keeping the total pressure and the partial pressure of oxygen constant. The diffusivities of O_2 and Mg (g) were varied by changing the type of inert diluent gas, argon or helium, mixed with oxygen. Figure 8 is a plot of the observed weight gain *vs* time in O_2-Ar and O_2-He atmospheres for a total pressure of 93,303 Pa and an oxygen partial pressure of 13,062 Pa. It is observed that the initial weight gain rate in helium is much higher than that in argon. The higher rate in He is consistent with the higher diffusivities of Mg (g) and O_2 in He as compared to that in Ar and is consistent with the prediction of Eq. [8]. In a second set, experiments were conducted at various total pressures for a constant oxygen partial pressure of 6531 Pa at 1391 K. Figure 9(a) is a plot of the observed weight gain

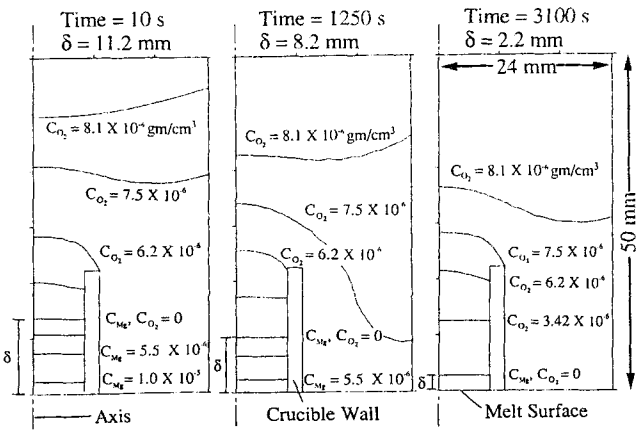

Fig. 10—Computed concentration profiles of Mg vapor and O_2 as a function of time for oxygen pressure of 3266 Pa, and total pressure of 93,303 Pa at 1391 K. The profiles show the movement of the oxygen front toward the melt surface with time. (Note: 1 g/cm³ = 10³ kg/m³.)

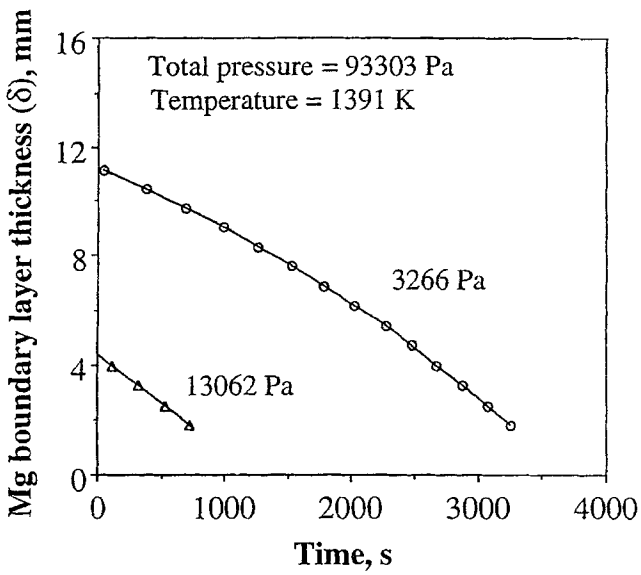

Fig. 11—Computed variation in the thickness of the Mg boundary layer (δ) during the initial stage of directed oxidation as a function of time for two different partial pressures of oxygen.

vs time for different total pressures. The results show that the weight gain rate increases with decreasing total pressure. Since the binary diffusivity of gases is inversely proportional to the total pressure, a decrease in the total pressure results in an increase in the diffusivities of O_2 and Mg (g) in argon and should result in an increase in weight gain rate. Figure 9(b) shows the variation in weight gain rate with diffusivity of oxygen. The results show a good correlation between weight gain rate and diffusivity and are consistent with the predictions of Eq. [8]. Thus, the results confirm diffusion-limited vaporization of magnesium during the initial stage of oxidation of Al-Mg alloys.

Figures 3, 8, and 9(a) show that the culmination of the initial stage of composite growth and the start of the incubation period is characterized by a sharp decrease in the weight gain rate. According to Vlach *et al.*,[5] this sharp decrease in the rate occurs due to the formation of a dense spinel layer which prevents magnesium vaporization and its subsequent oxidation. For alloy compositions between 0.2 and 10.4 mole pct Mg, the magnesium aluminate spinel is thermodynamically more stable than MgO at 1400 K.[14,16] The spinel layer can form at the melt surface by one of the following reactions:

$$4MgO + 2Al\ (l) = MgAl_2O_4 + 3Mg\ (l) \qquad [9]$$

$$Mg\ (l) + 2Al\ (l) + 2O_2 = MgAl_2O_4 \qquad [10]$$

Formation of spinel by Reaction [9] involves reaction of MgO with the alloy. Since MgO starts forming as soon as oxygen is introduced into the reactor, there is no reason to believe that the spinel formation should not start at the same time. If the spinel formation were to start as MgO forms, the cross section of the melt exposed to the oxygen atmosphere would decrease. However, the model does not take into account the decrease in the cross section of the melt surface, and yet, there is excellent agreement between the experimental observations and model predictions of weight gain *vs* time. If spinel formation occurs by way of Reaction [9], the end of the initial stage would correspond to a critical amount of MgO, required to form a spinel layer of certain thickness which would be impervious and stop further Mg vaporization. This entails that the same amount of MgO form at the end of the initial stage, irrespective of the experimental conditions of oxygen pressure and total pressure. However, it is observed that the weight gain at the end of the initial stage, which is a measure of the amount of MgO formed, is different for different oxygen pressures and total pressures, as evidenced from Figures 3 and 9(a), respectively. This indicates that the formation of spinel does not occur by Reaction [9] at a sufficiently rapid rate in the initial phase of oxidation.

The experimental results and the preceding discussion indicate that spinel formation involves the presence of oxygen at the melt surface. Figure 10 indicates that at the start of the initial stage of oxidation, the oxygen front is located far away from the surface, and hence, the spinel formation cannot occur during the initial stage of oxidation. However, Figure 10 also indicates that the oxygen front moves closer to the surface of the melt owing to a decrease in the magnesium vapor pressure as the initial stage progresses. Furthermore, Figure 11 shows that at the end of the initial stage, the thickness of the magnesium boundary layer, δ, is reduced to a small value and the oxygen front is present very close to the surface of the melt. The duration of the initial stage corresponds to the time required for the thickness of the magnesium vapor-inert gas layer, δ, to become sufficiently small so that oxygen can reach the melt surface and react with the alloy to form spinel.

IV. SUMMARY AND CONCLUSIONS

The initial stage of directed oxidation of Al-Mg alloys has been investigated both experimentally and theoretically. The weight gain with time during the initial stage was measured for different oxygen pressures. The oxygen pressures were established using inert gas-oxygen mixtures. The effect of diffusivity of oxygen and magnesium on the weight gain rate was examined by varying the external pressure and the nature of inert gas while maintaining the oxygen pressure constant. In the initial stage, MgO forms by vapor phase oxidation of Mg (g) and falls back on the

crucible. A mathematical model was developed for the vaporization of Mg from the Al-Mg alloy in a reactive oxygen-inert gas atmosphere. The model calculates the velocity, temperature, and concentration profiles in the reactor through numerical solutions of the equations of conservation of momentum, enthalpy, and concentrations of Mg (g) and O_2. The magnesium vaporization rate and the corresponding oxygen weight gain rate are calculated from the concentration profiles as a function of time. The predictions of the model are compared with experimental data to seek an improved understanding of the initial stage of the composite growth.

The predicted variation of the weight gain with time in the initial stage of oxidation agreed well with the experimental data. It is seen that at low oxygen pressures comparable to the equilibrium Mg vapor pressure over the Al-Mg alloy, the weight gain rate in the initial stage decreases with time, while at high oxygen pressures, the weight gain rate is independent of time. The weight gain rate in the initial stage also increases with the increase in oxygen pressure and oxygen diffusivity. These results confirm the reaction-enhanced gaseous diffusion-limited vaporization of Mg in the initial stage of oxidation of Al-Mg alloys. The thickness of the magnesium boundary layer decreases continuously with time as the alloy composition changes owing to magnesium vaporization. It is shown that the end of the initial stage corresponds to the time when the oxygen front essentially collapses onto the alloy surface.

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