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Mathematical Simulation of the Wettability of Al₂O₃ Substrate through Different Aluminum Alloys

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Abstract: The wetting process of a ceramic substrate (Al₂O₃) with and without carbon coating by means of aluminum-based alloys has been investigated. A mathematical simulation that predicts wettability in the systems under study is proposed, taking into account the diffusional effects of the used constituents. The prediction of the mathematical simulation is compared with the experimental results obtained for the same systems in question. From the results obtained, it was found that the wettability of a liquid droplet of aluminum and aluminum alloys on an alumina (Al₂O₃) substrate with and without carbon coating can be well represented by the proposed mathematical diffusion simulation. On the other hand, the control mechanism of the contact angle in relation to the deposition of a thin layer of carbon on the ceramic substrate (Al₂O₃) and the presence of metals such as La and Y in the aluminum alloy, give way to the formation of Al₄C₃, La₂O₃ and Y₂O₃ and these types of reaction help in the decrease of the contact angle.

Keywords: wettability; Al₂O₃ substrate; mathematical simulation; aluminum alloys; carbon coating; sessile drop



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1. Introduction

Metal-ceramic composites have been widely explored and developed in the past fifty years. The exploration of the wetting behavior of strengthened body and substrate could provide effective guidance for the preparation of new composite materials. If the wettability between the strengthened body and substrate is very poor, it will be hard to make it an effective compound without the wettability between them. Wetting of ceramic substrates by liquid metals is important for various applications such as coating, joining, and composite processing. Thus, interfacial phenomena between metals and ceramics are of great scientific and technological interest since the behavior of composite materials created by interfacial bonds is directly associated with the nature of the metal–ceramic interface. Specifically, wetting of ceramic surfaces by liquid metals is an important phenomenon in the production of composite materials where liquid infiltration into the ceramic and bond control play a very important role [1]. The aluminum-alumina system is a candidate with high potential for the creation of composite materials with a wide scale of possible applications due to its low density, coupled with high toughness and mechanical strength compared to monolithic alumina ceramics. However, it is well known that the wettability in many metal-ceramic-liquid systems is very poor, especially in systems where the ceramic is an oxide [2]. This is due to the high degree of ionic bonding that ceramic oxides present, which prevents their good wettability by a liquid metal, unlike ceramic systems such as nitrides or carbides, where the wettability of the ceramic by the metal is greater, as a consequence of the fact that the latter present a bond with a greater covalent character [3].

The mechanism of wetting liquid metals on ceramic surfaces is still under debate. It is well known that there is a thin oxide layer on the surface of the liquid metal. This oxide

layer has a significant effect on the determination of the wetting equilibrium angles [4–7]. Consequently, the diffusion of metal atoms through the oxide layer surrounding the surface of the liquid droplet is important, and affects the wetting kinetics. Similarly, the diffusion of metal atoms on a ceramic surface also plays an important role. Therefore, diffusion through the oxide layer and diffusion on the surface affect the wetting kinetics. In this study the wettability of Al₂O₃-based ceramics by different aluminum alloys has been experimentally analyzed by modifying the interfacial contact area between the metal and the ceramic by means of a thin layer of graphite. On the other hand, the experimental results are represented with the help of a mathematical model proposed by Zhou and Hosson [8], which is based on the difference of surface stresses between the equilibrium and non-equilibrium states of the wettability of the ceramic by the metal.

2. Description of the Mathematical Model

Wetting the surface energy difference between the equilibrium and non-equilibrium states contributes to the energy involved for diffusion. The surface energy difference ΔE_γ , is given by;

$$\Delta E_\gamma = \pi r^2 \gamma_1 (\cos \theta_e - \cos \theta) \tag{1}$$

where

r = is the radius of the atoms of the liquid

γ_1 = liquid surface tension

θ_e = contact angle in equilibrium

θ = non-equilibrium contact angle

Thermal vibrations of atoms on a solid surface or a solid layer are resistant to the wetting process in the diffusion mechanism. According to statistical physics, the probability that an atom jumps is given by

$$V = V_0 \exp \left[\frac{-Q}{KT} \right] \tag{2}$$

where

V_0 = Vibrational frequency of the atoms

Q = Activation energy of diffusion

K = Boltzmann’s constant

T = Absolute temperature

The jump of the liquid atoms of the network per second, which contributes to the wetting process, is equal to the difference between the jump of the atoms out of the liquid and the jump of the atoms inside the liquid.

$$\begin{aligned} \Delta V &= V_{OUT} - V_{IN} = V_0 \exp \left[\frac{-Q - \Delta E_\gamma}{KT} \right] - V_0 \exp \left(\frac{-Q}{KT} \right) \\ \Delta V &= V_0 \exp \left(\frac{-Q}{KT} \right) \left\{ \exp \left[\frac{\pi r^2 \gamma_1 (\cos \theta_e - \cos \theta)}{KT} \right] - 1 \right\} \end{aligned} \tag{3}$$

Each jump distance is about the atomic distance. On the other hand, the velocity of motion of the liquid droplet contact line on a solid surface is equal to the product of $2r$ and ΔV . By introducing the Frequency factor $D_0 = (2r)2 V_0$ into Equation (3), the velocity of motion V_x can be derived as follows:

$$V_x = \frac{D_0}{2r} \exp \left[\frac{-Q}{KT} \right] \left\{ \exp \left(\frac{\pi r^2 \gamma_1 (\cos \theta_e - \cos \theta)}{KT} \right) - 1 \right\} \tag{4}$$

According to the geometry of the wetting process, as shown in Figure 1.

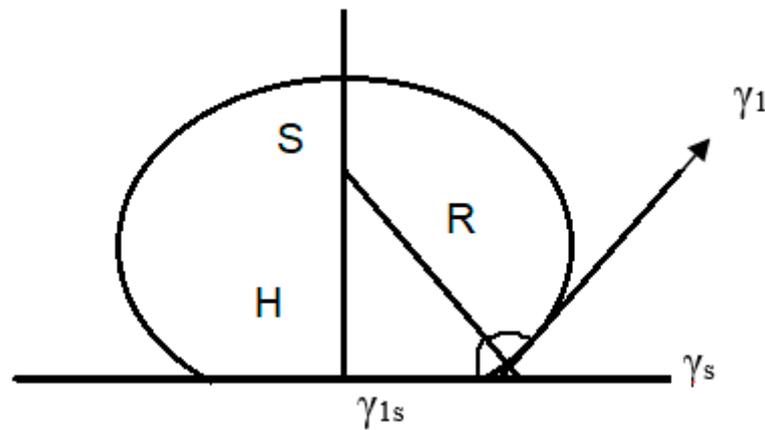


Figure 1. Liquid drop on a solid surface.

The velocity of motion V_x can also be described by Equation (5) in the x-direction.

$$V_x = \frac{d(R\sin\theta)}{dt} = -\frac{R}{2 + \cos\theta} \frac{d\theta_x}{dt} \tag{5}$$

Integrating Equation (5) with respect to θ , then introducing the expression of V_x from Equation (4), it will have the time dependence with respect to the contact angle as follows:

$$t = \int_{\theta}^{\theta_0} \frac{R}{(2 + \cos\theta) V_x} d\theta$$

$$t = \int_{\theta}^{\theta_0} \frac{R \left(\frac{2r}{D_0}\right) \exp\left[\frac{Q}{KT}\right]}{(2 + \cos\theta) \left\{ \exp\left[\frac{\pi r^2 \gamma_1 (\cos\theta_e - \cos\theta)}{KT}\right] - 1 \right\}} d\theta \tag{6}$$

where

- Q = Activation energy
- K = Boltzmann’s constant
- T = Absolute temperature
- γ_1 = Surface tension of the droplet
- θ_e = Equilibrium angle of wetting
- R = Drop radius
- D_0 = Frequency factor
- r = Radius of the atom

In the case of diffusion through an oxide layer, the activation energy, Q, includes the atom migration energy and the energy of creating a vacancy. Equation (6), the general equation for the diffusion model of wetting kinetics, is valid for both cases, surface diffusion and diffusion through an oxide layer [8].

3. Materials and Methods

3.1. Substrate Preparation

The substrates used are polycrystalline Al_2O_3 with a purity of 99.6% and an approximate thickness of 0.64 mm. With the aid of a diamond disk cutter, small squares of approximately 1 cm × 1 cm on each side were cut. After cutting, the substrates were cleaned by agitation in an ultrasonic bath with acetone for 40 min to remove impurities and grease. Where required, 1 to 3 layers of carbon was deposited on the substrate by a steam deposition process, and each deposition cycle was approximately 45 s, which resulted in a thin layer of carbon approximately 1 μm thick. Seven different systems are studied and the difference between them is presented in Table 1.

Table 1. Identification of the samples used in the experimentation.

| Sample | System | Carbon-Coated Substrate |
|--------|--|-------------------------|
| A1 | Al-Al ₂ O ₃ | Control |
| AC1 | Al-Al ₂ O ₃ | 1 cycle C deposition |
| AC3 | Al-Al ₂ O ₃ | 3 cycles C deposition |
| AY | Al-3% Y-Al ₂ O ₃ | No |
| AL | Al-2.5 La-Al ₂ O ₃ | No |
| ACY | Al-3% Y-Al ₂ O ₃ | 3 cycles C deposition |
| ACL | Al-2.5 La-Al ₂ O ₃ | 3 cycles C deposition |

These compositions were considered because the Al alloys with Y and La belong to the composition with the lowest melting point in the respective phase diagram, which means the eutectic composition. The alloys were prepared by vacuum casting, using Al, La and Y with a purity greater than 99.5%. The alloy compositions were the eutectic ones of the Al-La (77.2 at. % La and melting point of 521 °C) [9] and Al-Y (75 at % Y and melting point of 955 °C) [10] systems. The use of these alloying elements was also considered because they have a higher affinity for oxygen than aluminum, which may favor the wettability of the ceramic by the metal [11].

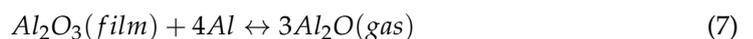
3.2. Wettability Experiments

The wettability experiments known as Sessile Drop experiments were developed using an induction heat generator (Lepel High Frequency Lab. Inc., Model T-30-3DF-TL, Chicago, IL, USA), which is used to heat the sample. The experiments were conducted in a water-cooled stainless steel chamber, with vacuums of 10⁻⁴ to 10⁻⁵ Pa. For all systems, the working temperature was 1300 °C for a time that varied between 0 and 7200 s. The drop profiles were recorded in-situ with the aid of a video camera (Canon L2, Tokyo, Japan), as a function of time. The temperature of the liquid metal was measured with the aid of an infrared light camera (Canon L2, Tokyo, Japan) as a function of time (Ircon, Inc., Model MR-OR10-19C, Niles, IL, USA). Contact angle measurements were made directly from the images obtained from the digital camera (Olympus 350, Tokyo, Japan) with the aid of a protractor.

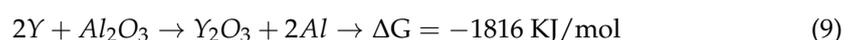
4. Results

4.1. Contact Angle Variation

Figure 2 shows the experimental results of the variation of the contact angle as a function of time, at a constant temperature of 1300 °C, obtained for all the systems proposed here. As can be seen in this figure, in all cases, it is during the first stage (from $t_0 = 0$ to $t_1 = 600$ s) where there is a greater speed in the decrease of the contact angle. This behavior has previously been well documented [12], and the control here is said to be primarily due to the deoxidation of the droplet, which occurs primarily by the reduction of the thin film formed at the liquid–ceramic interface with the production of Al₂O in gaseous form as described in the following reaction [13].



During the second stage between t_1 and t_2 ($t_2 = 4500$ s), the wetting rate decreases considerably. However, it is at this stage that the minimum contact angle values are reached for all samples. This has also been previously documented [14–18] and the behavior has been explained by the occurrence of different chemical reactions taking place at the metal–ceramic interface between the alloying elements (La, Y) with the oxygen of the medium and C with Al, leading to the formation of the products described below:





During the third stage (times greater than 4500 s), the values of the contact angle remain practically constant in all cases, which may be due to the fact that the distances for diffusion to take place are already greater, thus preventing greater wettability of the ceramic by the liquid metal.

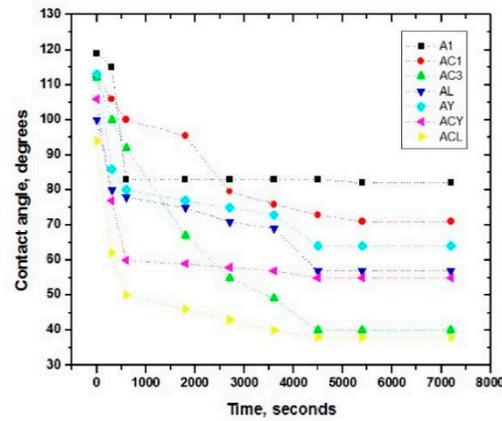


Figure 2. Variation of liquid droplet contact angle as a function of time for all systems.

Figure 3 shows the corresponding drop profiles for all samples, taken when the time of the drop at 1300 °C was 4500 s, which is the moment where the angle of the drop decreases considerably. Here it is very well appreciated how the presence of carbon on the surface of the alumina substrate, as well as the presence of La and Y in the aluminum alloy, favor considerably the decrease of the contact angle between the liquid aluminum droplet and the substrate. This as, already explained, is due to the different chemical reactions that take place at the liquid metal–solid substrate interface.

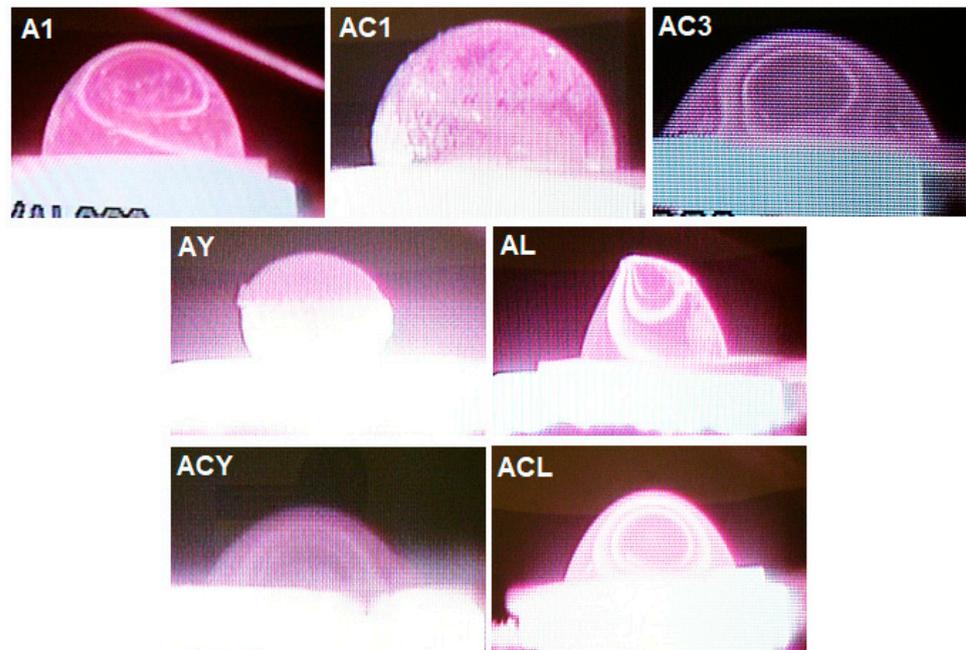


Figure 3. Profiles of aluminum alloy liquid droplet on alumina substrate. Temperature from 1300 °C to 4500 s exposure.

4.2. Metal–Ceramic Interface

Observations of the interfacial region between the metal and the ceramic substrate were carried out using Scanning Electron Microscopy SEM (Jeol, S-4700, Tokyo, Japan). These were carried out after removing the solidified aluminum droplet from the ceramic substrate in all samples (experimental conditions: $T = 1300\text{ }^{\circ}\text{C}$, $t = 4500\text{ s}$). Figure 4a–c shows the formation of ridges on the surface of the ceramic substrates (Al_2O_3) that reach the edge of the liquid aluminum. Therefore, it is suggested that there is a reactive liquid metal–ceramic substrate interface. The length of the grooved zone is approximately 50, 55 and $60\text{ }\mu\text{m}$ for samples A1, AY and AL, respectively.

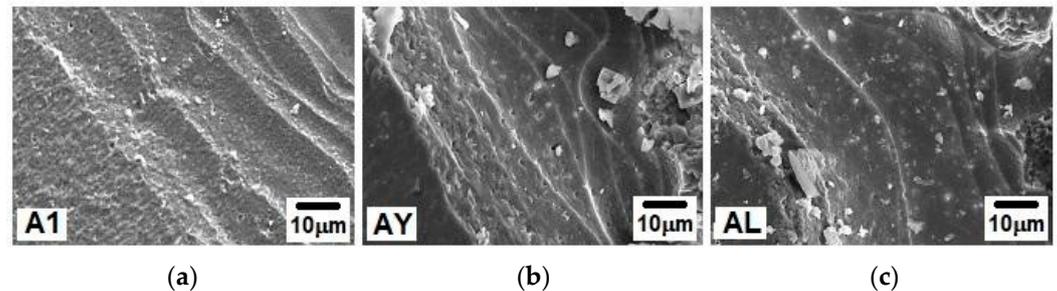


Figure 4. Micrographs showing the advance of the ridges of the specimens. (a) A1, (b) AY y (c) AL at a temperature of $1300\text{ }^{\circ}\text{C}$ during 4500 seg.

This distance, observed in Figure 4b,c, represents the advance of the liquid droplet spreading on the ceramic substrate; therefore, a larger distance from the grooved zone represents a better wettability in the system, which makes it evident that the AL sample presents a better wettability. On the contrary, shorter distances of the grooves formed on the substrate, as shown in Figure 4a for sample A1, indicate poor wettability.

This may be due to the fact that the reactions 11 and 12 take place between the alloying elements contained in the aluminum alloys and the oxygen at the liquid metal–ceramic substrate interface, thus having a chemically reactive interface, so there is a chemical attack on the substrate, which delimits very well the grain boundaries of the ceramic substrate (Figure 5).

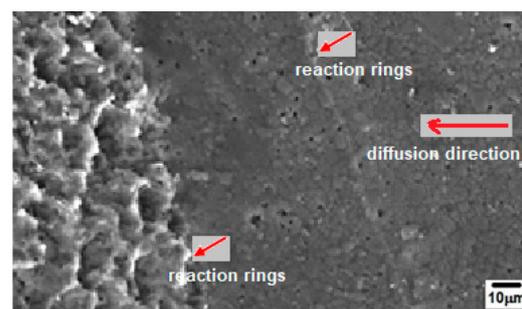


Figure 5. Micrograph of the cross-section of sample AC3.

4.3. Mathematical Simulation

With the help of Equation (6), which corresponds to the proposed diffusion model, the wetting kinetics for the systems studied here is simulated. The values considered for the simulation corresponding to the frequency factor, activation energy and surface tension of aluminum on polycrystalline Al_2O_3 are as follows: $D_0 = 0.048\text{ m}^2\text{ s}^{-1}$, $Q = 8.67 \times 10^{-19}\text{ J K}^{-1}\text{ at}^{-1}$ and $\gamma_1 = 0.914\text{ N m}^{-2}$ respectively and were obtained from the work of Kingery [19].

The simulation results for the contact angle as a function of time at a temperature of $1300\text{ }^{\circ}\text{C}$ for the systems studied are shown in Figure 6. This figure shows that as the time

increases, the wetting angle decreases significantly. According to this simulation, around 4500 s is the time to obtain the minimum values of the wetting angle for almost all the samples. The predictions obtained by applying the diffusion model using Equation (6) of the wetting kinetics are very close to the experimental results, since the behavior is very similar in each of the systems, both mathematically modeled and experimentally obtained. In the case of the A1 system, there is a sharp decrease in the contact angle after 1200 s. Different researchers have reported the formation of Al_4C_3 as being responsible for the enhancement in the contact angle [20,21].

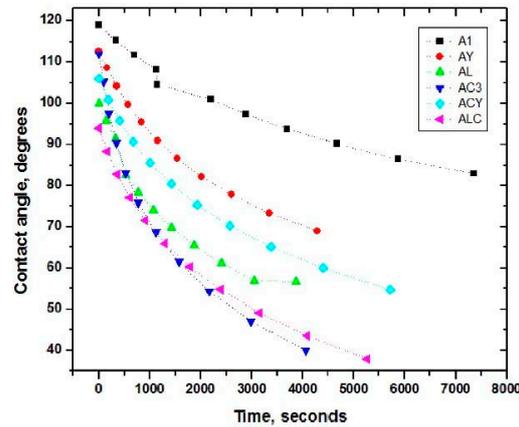


Figure 6. Variation of the liquid drop contact angle as a function of time for all systems, calculated with Equation (6) at a temperature of 1300 °C.

To get a better view of the predictions made with the mathematical model, a system is taken at random and the results of the model are compared with the experimental results. Thus, Figure 7 is presented, which corresponds to the Al- Al_2O_3 (AC3) system. The following values of properties of the liquid aluminum wetting the ceramic substrate were used in the mathematical model represented by Equation (6); $D_0 = 0.048 \text{ m}^2 \text{ s}^{-1}$, $Q = 8.67 \times 10^{-19} \text{ J K}^{-1} \text{ at}^{-1}$, $\gamma_1 = 0.914 \text{ N m}^{-2}$ and $\theta_e = 40^\circ$. This figure shows the variation of the contact angle as a function of the residence time at 1300 °C of the metal on the ceramic substrate. According to Figure 7, the behavior of the curve obtained by the mathematical model is very similar to the experimental curve, and for this reason it can be noted that the prediction of the mathematical model is very accurate, and this can facilitate the prediction of the behavior of the wettability of aluminum on alumina-based substrates under different processing conditions.

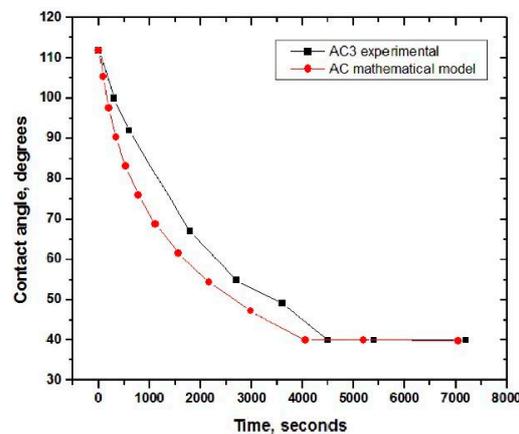


Figure 7. Contact angle curves as a function of time, experimental and calculated with Equation (6) for the wetting of a liquid drop of aluminum on a carbon-coated Al_2O_3 surface at a temperature of 1300 °C.

5. Conclusions

The Sessile droplet technique has been used to study the effect of carbon on the contact angle between an alumina substrate and a droplet of aluminum alloys. One of the primary bases for obtaining large contact angles during the first stage of wetting kinetics is given by the oxidation of the droplet, so it was found that the first diffusional mechanism over time can be associated with the interactions between the Al_2O_3 film formed at the interface between the liquid metal and the ceramic substrate with the formation of Al_2O in gaseous form, which helps to have a decrease in the contact angle. During the second stage the diffusional control mechanism can be related to the addition of alloying elements such as lanthanum and yttrium, causing them to react with oxygen at the interface, leading to the formation of oxides of these elements (La_2O_3 and Y_2O_3). Likewise, the deposition of a thin layer of carbon on the ceramic substrate (Al_2O_3) gives way to the formation of aluminum carbide (Al_4C_3), and both types of reactions help in the decrease of the contact angle. Regarding the mathematical model based on diffusional aspects to predict the wetting kinetics of a ceramic substrate by a liquid drop in the present work, it can be commented that it describes well, in general terms, the wetting process.

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