Wettability of Al_2O_3-MgO Substrates by Molten Aluminum

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A large amount and many kinds of refractories are used in the metallic smelting process. As the refractories are generally utilized at a high temperature in a metallic smelting process, those are reusable enough in a low temperature process, e.g., aluminum alloy casting process. The casting process often needs dressing materials, which are sprayed on the surface of mold and dried by heating. The sprayed thin film formed on the surface of the mold enables the repetitive use of the mold due to prevention of direct contact between the mold and molten aluminum. Therefore, the wettability of dressing materials by molten aluminum is an important factor controlling the longevity of the mold. Because ceramic oxides such as alumina, magnesia, and silica are widely used as the refractories of a metallic smelting process, the wettability of the ceramic oxides by molten aluminum has been studied extensively [1]. However, wettability between molten aluminum and ceramics consisting of two or more oxide system has not been well understood. This study focused on Al_2O_3-MgO refractories that have been widely used in steel smelting. In order to obtain a basic data for the refractories reused as an aggregate of dressing materials, the wettability of Al_2O_3-MgO substrates by molten aluminum was investigated.

Cylinders of pure aluminum (99.99mass%) with 5 mm diameter and 6 mm height were mechanically ground using an emery paper (#800) and soaked in a sodium hydroxide solution to obtain a clean surface. Al_2O_3-MgO ceramics were prepared as substrate materials where the powders of alumina and magnesia were mixed in an alumina pot mill, followed by press with 150 kgf/cm^2, sintering at 1873 K and polishing with emery paper (#1500). Thus three kinds of substrates which were of Al_2O_3 free from MgO, Al_2O_3-10mass%MgO, and Al_2O_3-28mass%MgO were prepared. A commercial alumina, which was 99.5% pure and dense, was also prepared as substrate in this study for comparison.

Figure 1 shows an assemble system for the wettability measurement.

The system composed of an electric furnace, a vacuum pump, a tungsten filament lump, and a camera to take a picture of aluminum droplet. The transparent silica tube of 30 mm diameter was employed as a core tube of the furnace. Wettability measurement was carried out by the sessile drop method. The core tube was evacuated down to 1.5 Pa and heated to the measurement temperature. Pictures of aluminum droplet were taken at intervals of five minutes and the contact angle between aluminum droplet and substrate was directly measured from the negative film.

X-ray diffraction patterns of the three kinds of Al_2O_3-MgO substrate are shown in figure 2. Substrate of Al_2O_3 is of α-alumina and that of Al_2O_3-28mass%MgO totally spinel phase of $MgAl_2O_4$. Substrate of Al_2O_3-10mass%MgO is of a mixture of α-alumina and the spinel phases. The spinel phase of Al_2O_3-28mass%MgO is in agreement with stoichiometric law as indicated in the phase diagram [2]. On the other hand, the spinel phase of Al_2O_3-10mass%MgO is non-stoichiometric and consists of 20mass%MgO as reported previously [3].

Figure 3 shows change in contact angle of the molten aluminum and substrates with holding time where the plotted value is an average of several measurements. Contact angles from Al_2O_3 substrate are in agreement with those reported in the literatures [4,5]. No change in contact angle with holding time for Al_2O_3-10mass%MgO can be observed although there is an appreciable change of the angle, depending on the holding temperature when held at 1023 K to 1223 K. A 1273 K, the angle decreases with holding time and finally reaches 100 deg. The contact angle for the Al_2O_3-28mass%MgO substrate is 150 deg, and does not change with both holding time and temperature.

It is known that surface condition of substrate generally influences on the contact angle, i.e., the wettability. There were many pores in all substrates because sintering additives was not added to avoid pollution with the impurities. Contact angle using a commercial alumina block with few pores was measured to compare the self-made ones. As shown in figure 4, the same tendency with the self-made Al_2O_3 substrate is observed. Therefore the decrease in contact angle is probably governed by the other factors than the surface pore.

A vivid metallic luster was observed at the surface of the molten aluminum when the substrates of Al_2O_3 were held at 1223 K and 1273 K and of Al_2O_3-10mass%MgO at 1273 K. Under other experimental conditions, the metallic luster, which was observed only at an initial stage of holding, diminished with increasing the holding time. Oxidation of aluminum surface is generally unavoidable because aluminum is prone to be oxidized by oxygen. The formed oxide film is expected to prevent an extension of droplet. However, there is a possibility that the oxide film, i.e., the alumina film is removed by the following reaction with molten aluminum [4].

$$Al_2O_3(s) + 4\,Al(l) = 3Al_2O(g) \quad (1)$$

Table 1 shows partial pressure of Al_2O at equilibrium. It is seen that the reaction is favored at higher the temperature. The metallic luster observed in Al_2O_3 substrate at high temperatures of 1223 K and 1273 K may result from the removal of the alumina film through reaction (1), bringing about a progress of wettability to show the decreased contact angle (see upper row of figure 3). Furthermore, partial pressure of Al_20 about 10^{-3} Pa is a critical pressure to remove the alumina film of droplet (see equation (1) and table 1).

The oxide film may not be composed only of pure alumina when the substrate contains MgO. The spinel film formed on the droplet's surface must influence on the wettability provided that it is thermodynamically stable. It is necessary, therefore, to consider the following reaction in order to understand stability of the spinel film.

$$MgAl_2O_4(s) + 6\,Al(l) = Mg(g) + 4\,Al_2O(g) \quad (2)$$

$$MgAl_2O_4(s) + 4\,Al(l) = MgO(g) + 3\,Al_2O(g) \quad (3)$$

Because MgO is thermodynamically more stable than Al_2O_3, MgO is unlikely reduced to Mg gas; therefore, the removal of the spinel film by reaction (2) cannot be expected. In regard to reaction (3), the amount ratio of generated MgO gas and Al_2O gas must be 1:3. The calculated equilibrium partial pressures of Al_2O of reaction (3) are three or four orders lower than those of reaction (1) (see table 2). This indicates that spinel is thermodynamically more stable than alumina, that is, the spinel film is hardly removed. In fact, the droplet of Al_2O_3-28mass%MgO substrate did not show a metallic luster. Moreover, the contact angle had a very high value of 150 deg (see figure 3). These are consistent with the thermodynamic consideration, which requires higher temperature than for removing the spinel film.

The Al_2O_3-10mass%MgO substrate also consists of the spinel phase, which is non-stoichiometric owing to the insufficient content of MgO [3]. In other words, the spinel phase is a solid solution having excess Al_2O_3. Therefore, the spinel phase changes to separate itself into Al_2O_3 and a spinel phase that contains more MgO during holding at high temperatures [6], as would be expected from the phase diagram [2]. From this point of view, the Mg^{2+} ions in the Al_2O_3-10mass%MgO substrate hardly contribute to the spinel formation on the droplet's surface. As a result, the oxide film does not consist of the spinel phase but the alumina phase. The alumina film formed on the Al_2O_3-10mass%MgO may be removed during holding at a high temperature through the reaction (1). This is consistent with that the contact angle decreases (see figure 3) and the metallic luster was observed at 1273 K.

Finally, two data books [7,8] were referred in the above thermodynamic calculation, and the thermodynamic data of the non-stoichiometric spinel phase has been replaced by the stoichiometric one because there has been no thermodynamic data of the non-stoichiometric spinel phase.

The present work indicates that the oxide film formed on the surface of molten aluminum plays an important role in the wettability between metal and ceramic. Substrate of Al_2O_3-20mass%MgO, which consists only of the stoichiometric $MgAl_2O_4$ spinel particles, exhibits high contact angles about 150 deg in a temperature range of 1023 K to 1273 K. The spinel film may be formed on aluminum surface and obstructs the progress of wetting. For substrate of Al_2O_3-10mass%MgO consisting of α-alumina and spinel phases, the contact angle has almost constant value of 140 to 150 deg during holding at temperatures lower than 1223 K. This is due to the formation of alumina film on the surface of aluminum droplet. On the other hand, the contact angle gradually decreases with time at a high temperature of 1273 K due to the removal of alumina film.

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Table1 Partial pressure of Al_2O gas calculated based on equation (1).

Temperature / K	p_{Al_2O} / Pa
1023	2.7×10^{-7}
1123	1.2×10^{-5}
1223	4.1×10^{-4}
1273	2.0×10^{-3}

Table2 Partial pressure of MgO and Al_2O gas calculated based on equation (3).

Temperature / K	p_{MgO} / Pa	p_{Al_2O} / Pa
1023	3.0×10^{-11}	9.1×10^{-11}
1123	4.4×10^{-9}	1.3×10^{-8}
1223	2.6×10^{-8}	7.8×10^{-8}
1273	1.7×10^{-6}	5.1×10^{-6}

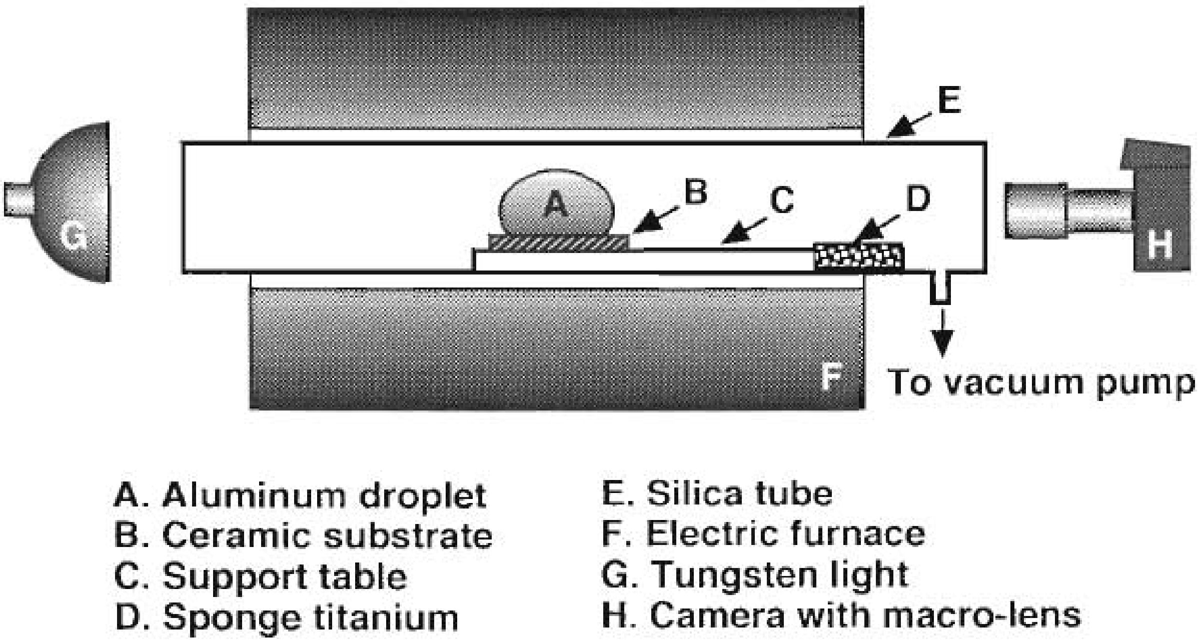

Fig.1 Schematic view of the experimental apparatus.

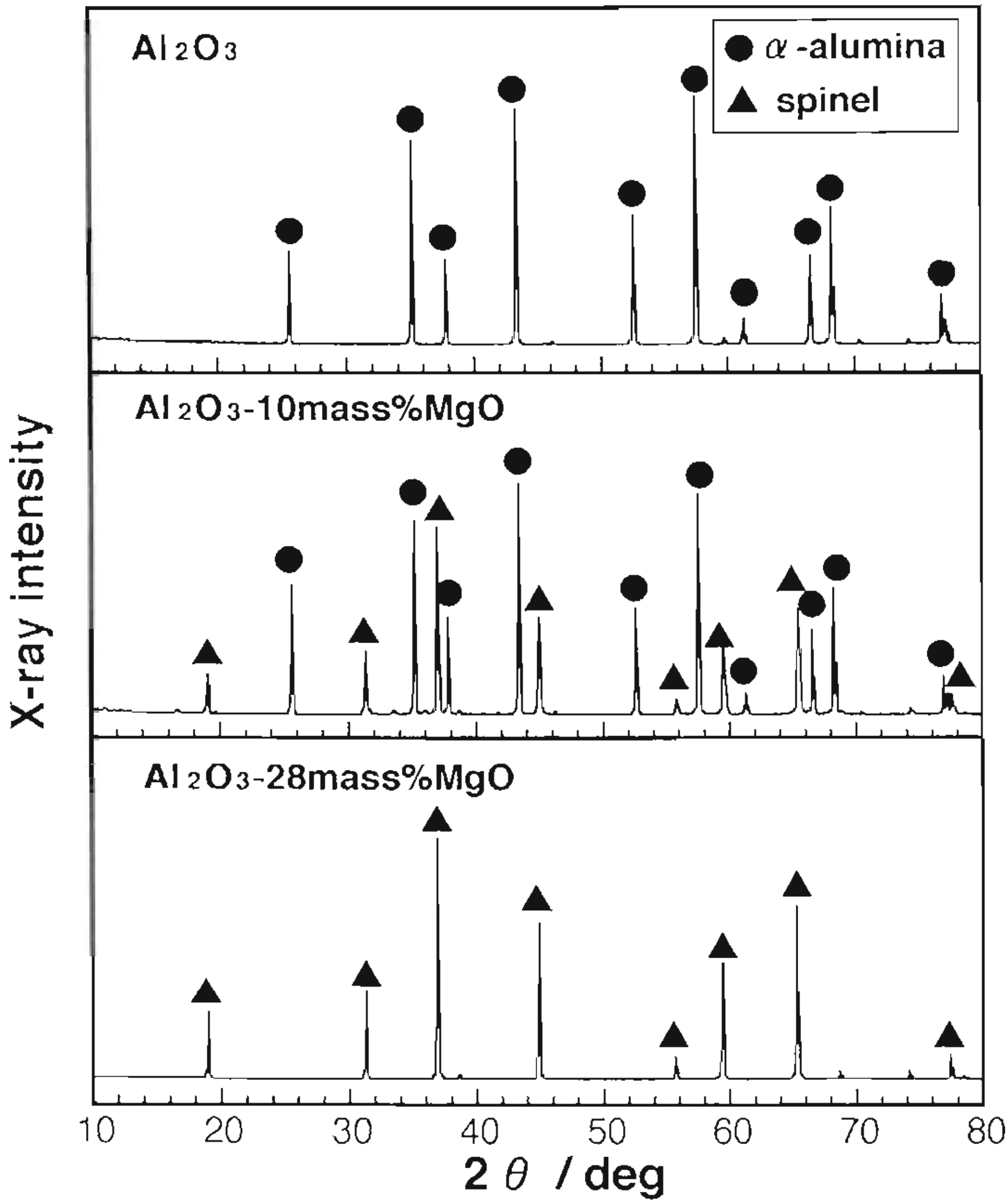

Fig.2 X-ray diffraction patterns of Al_2O_3-MgO substrates.

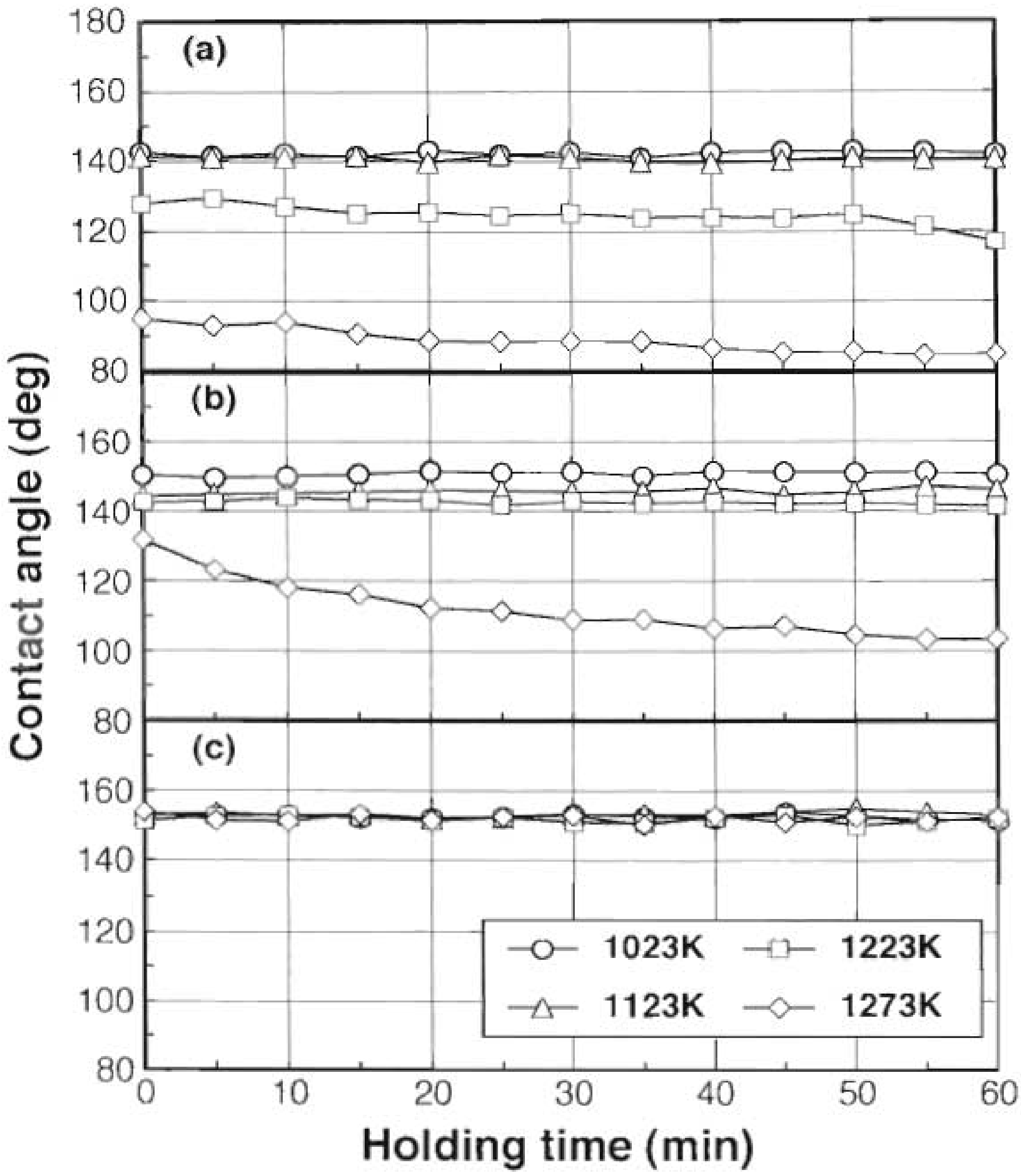

Fig.3 Change of contact angle with holding time in substrates of (a) Al_2O_3, (b) Al_2O_3-10mass%MgO, and(c) Al_2O_3-28mass%MgO.

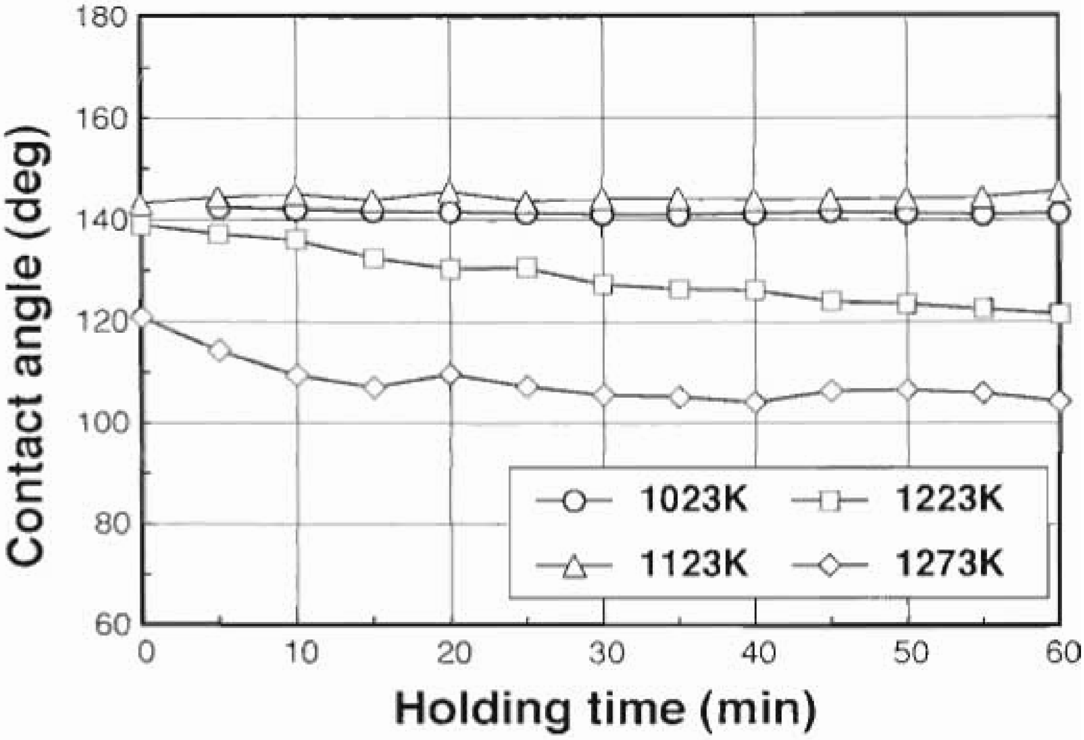

Fig.4 Change in contact angle with holding time in commercial alumina substrate.