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Reactive wetting in liquid magnesium/silica and magnesium/silicon systems

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ABSTRACT

The reactive wetting of SiO_2 and Si by molten Mg in a flowing Ar atmosphere was studied using an improved sessile drop method. The initial contact angles in the Mg/SiO_2 system decreased from 56° to 35° as temperature increased from 973 K to 1073 K, and they decreased very rapidly with time during isothermal holding. The interfacial reaction led to the formation of a distinct reaction zone, consisting mainly of a thin Mg_2Si layer, an MgO layer, a periodic alternatively arranged MgO and Mg_2Si layer, and an aggregated Mg_2Si–MgO mixture layer. The formation mechanism of these complex structures was discussed based on thermodynamic and kinetic considerations. Moreover, the effect of the interfacial reaction on the wetting improvement was examined and the primary contribution was ascribed to the formation of Mg_2Si at the interface, which was further demonstrated by the result in the Mg/Si system.

1. Introduction

In recent years, SiC–reinforced magnesium-matrix composites have received great attention because of outstanding properties such as low density, high specific strength and stiffness, and thus have potential applications in aerospace and automotive industries [1–4]. These composites are usually fabricated by way of liquid routes such as stir casting, squeeze casting and infiltration, in which the wettability between SiC and the Mg-matrix plays a significant role in determination of the ease of the process, the bonding quality and even the final properties of the composites [5].

As known, a silica layer was usually naturally present or artificially introduced at the SiC surface and was presumed to improve the wettability of SiC by molten Mg or Mg-containing alloys [6–8]. For instance, Epicier et al. [6] reported that coating the surface of SiC particles with silica via controlled oxidation in air was a very efficient treatment to promote wetting of these particles by liquid magnesium. Pressureless melt-infiltration of such pre-oxidized SiC particles was observed, while untreated particles were rejected from the Mg melt. Alternatively, Kaneda and Choh [2] fabricated SiC reinforced Mg-matrix composites by applying a spontaneous infiltration technique using SiO_2 as an infiltration agent in the Mg–SiC preforms. They suggested that the spontaneous infiltration was caused by the improvement of the wettability between the magnesium melt and the SiC particles, which resulted from the Mg–SiO_2 reaction at the infiltration front. However, the intrinsic wettability of SiO_2 by Mg, to the authors' knowledge, was seldom evaluated. Fritze and Nientit [9] might be the rare ones, who investigated the wetting of a polycrystalline SiO_2 substrate by a molten Mg alloy (containing 2–3 wt.% Ag, 2 wt.% Nd and Pr, 0.4–1 wt.% Zr and max. 0.4 wt.% impurities such as Zn, Fe and Mn) during continuous heating at a rate of 25 K min^{-1} in a contact mode, i.e., the Mg alloy was pre-placed on the SiO_2 substrate and then the couple was heated together from room temperature to the desired testing temperature in an Ar atmosphere. By such a way, they reported contact angles of 79° at 983 K and 35° at 1123 K. Nevertheless, these angles could not represent the intrinsic wettability of this system, since, on the one hand, the prior reaction between the Mg alloy and the SiO_2 substrate during heating was hardly avoided, and on the other, the oxidation of the Mg alloy at relatively low temperatures and the intense evaporation of Mg at high temperatures ($T > 1073$ K) would greatly affect the measurement of the contact angle, as we have demonstrated before [10], which, however, was not taken into account in their study.

In this study, we investigated the wetting of SiO_2 by molten Mg at 973–1073 K using an improved sessile drop method. The effect of the chemical reaction on the wettability and the formation mechanism of the interfacial microstructures were discussed. The results are expected to be valuable to the development of the Mg-matrix composites using naturally or artificially oxidized silicon carbide as reinforcement or using SiO_2 as a reactant.

2. Experimental procedure

The SiO_2 substrates used were in a purity of ~99.99 wt.% and dimensions of 20 mm × 20 mm × 2 mm. One side of their

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surfaces was polished to less than 9 nm (R_a) by the supplier. The Mg ingot (99.99 wt.%) was cut into small pieces weighing about 50–55 mg. Both the substrate and the Mg piece were ultrasonically cleaned in acetone for three times prior to wetting test.

Wetting was performed using an improved sessile drop method [11] in a stainless-steel furnace under an Ar (99.999% purity) atmosphere at a flow rate of 0.5 l min^{-1}. The pressure in the furnace was controlled to be constant at 0.12 MPa. The Ar gas was purified by passing through a magnesium (99.9 wt.%)-containing furnace at 673 K, a dehydrating tube filled with molecular sieves and finally an oxygen-absorption tube filled with palladium-type adsorbents in order to reduce water and oxygen levels before it was introduced to the furnace when the testing temperature was reached. After the temperature and the atmosphere were stabilized, the Mg specimen, previously stored in a foldable stainless-steel bellow outside the furnace, was introduced to an alumina dropping tube with a small hole of 1 mm in diameter at the bottom. The inner surface of the alumina tube was pre-attacked by molten Mg before it was used for the wetting test, and therefore the pollution of Mg by its reaction with the tube during the short dwells (30–40 s) for melting was minimized. The molten Mg was then extruded through the small hole by slightly decreasing the gas pressure in the furnace, making it lower than that in the alumina tube, and the initial oxide film covering the Mg surface was removed. The spreading of the drop was recorded using both a video camera at a rate of 60 frames/s and a normal charge-coupled-device camera at a maximum rate of 2 frames/s. The captured images were analyzed using a drop analysis program, in which contact angle (θ), contact diameter (D) and drop height (H) could be directly obtained.

After cooling at a rate of 10 K min^{-1}, selected samples were cut and polished for microstructural observation using a scanning electron microscope (SEM, Evo18, Carl Zeiss, Germany) equipped with an energy dispersive spectrometer (EDS). The phases at the interface were identified by X-ray micro-diffraction (XRD, D8 Discover with GADDS, Bruker AXS, Karlsruhe, Germany) using a probe of 100-μm beam diameter.

3. Results

3.1. Wetting behavior

Fig. 1 shows the variations in contact angle and contact diameter with time for molten Mg on the SiO_2 surface at temperatures between 973 and 1073 K. Wetting stages can be characterized according to the changes in the contact angle and contact diameter. At low temperatures (973–1023 K), the wetting could be characterized by two stages: (i) the spreading stage, in which the contact diameter increases while the contact angle decreases; (ii) the pinning stage, in which the contact diameter remains almost constant while the contact angle decreases due to the continuous Mg evaporation and infiltration or diffusion toward the bulk of the substrate, as will be analyzed in Section 3.2. However, the liquid front area was usually found to deform after a certain time of the spreading, making further measurement of the contact angle meaningless. Representative images given in Fig. 2 show these changes. At high temperatures (1048–1073 K), the pinning stage seemed absent since the drop immediately moved to an irregular shape after a very rapid spreading. The duration for the spreading stage decreased while the spreading rate increased remarkably as temperature increased. The initial contact angles were between 56° and 35°, decreasing with increasing temperature. Generally speaking, SiO_2 is well wetted by molten Mg and the wettability improves with increasing temperature.

3.2. Interfacial microstructures

Fig. 3 shows typical cross-section microstructures in an Mg/SiO_2 sample after wetting at 973 K for 180 s. As indicated, the reaction zone extended out of the triple line. Some irregular lump phases, discontinuously distributed at or near the liquid/solid interface, were identified to be Mg_2Si by EDS and micro-XRD analyses. According to the morphology and distribution of the reaction products, the reaction zone can be roughly divided into four layers (see Fig. 3). The first layer was adjacent to the drop and rich in Mg and Si, consisting mainly of fine Mg_2Si grains, which continuously distributed at the interface (see Fig. 3c). The second layer was rich in

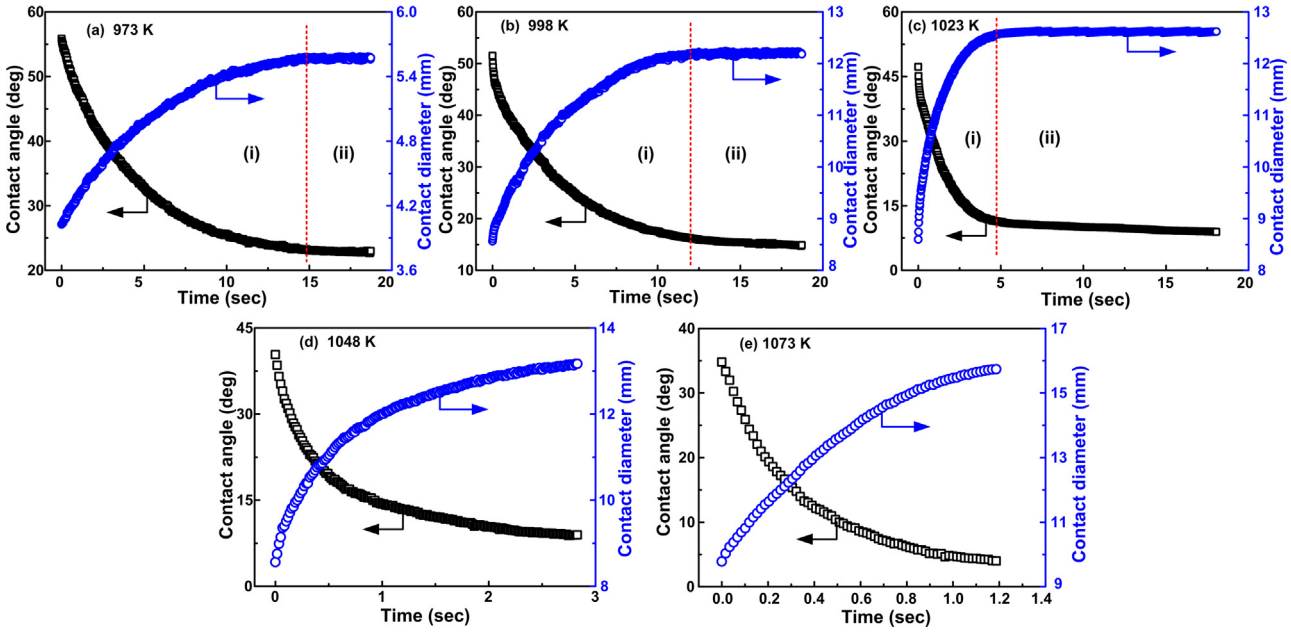

Fig. 1. Variations in contact angle and contact diameter with time for molten Mg on the SiO_2 surfaces during isothermal dwelling at 973–1073 K.