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The spreading kinetics and precursor film characteristics of Zr-based alloy melt on W substrate

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ABSTRACT

The wettability and spreading kinetics of Zr-based alloy melt on W substrate were evaluated using the modified sessile drop method under ultrahigh vacuum. The alloy melt wets the substrate well and the spreading kinetics indicates that drop spreading is mainly controlled by the viscous friction. The drop spreads rapidly and the spreading follows the hydrodynamic model and Jiang's empirical formula. The spreading of the drop shows little interaction with the precursor film, which is generated by diffusion. After the initial incubation period, the equilibrium contact angle stabilizes at about 29°, and the precursor film spreads linearly with the square root of time.

1. Introduction

Bulk metallic glass composites (BMGCs) have been studied and applied widely, among which the W reinforced BMGCs with superior mechanical properties are considered to be the most promising materials [1–4]. Accordingly, Zr-based BMGCs reinforced with W balls [1], W fibers [2,3] as well as porous W [4] have been developed and present excellent properties, which largely depends on the appropriate wettability of W by the liquid alloys. The wetting behaviors between W and Zr-based alloys have been studied and show good wettability thermodynamically [5,6]. Nevertheless, it is essential to be feasible kinetically, i.e., rapid wetting is necessary to avoid interfacial reaction in preparing composites. Besides, the appearance of the precursor film usually indicates good wettability [7,8]. However, only limited works dealt with the precursor film in the metal–metal wetting couples at high temperatures, which greatly confines our further study on the improvement of the wettability.

For these reasons, the spreading kinetics and the precursor film characteristics deserve to be deeply studied. Shen et al. [8,9] modified the traditional sessile drop technique and studied the spreading kinetics widely as well as the precursor film mainly in the metal–ceramic system. Besides, our previous works show that the mechanical properties of W/Zr–Ti–Cu–Ni–Be BMGCs are closely related to the interfacial bonding. Minor Nb addition could improve the interfacial structure effectively [10,11]. For further improvement of the mechanical performance, the wetting behavior of minor Nb alloying Zr–Ti–Cu–Ni–Be melt on the W substrate was studied in this work to confirm the driven force of the drop spreading and the relationship between the precursor film and the droplet, and further provide an essential feasibility research and theoretical guideline for composite preparation.

2. Experimental

The $Zr_{38.88}Ti_{12.90}Cu_{11.48}Ni_{9.77}Be_{23.97}Nb_{3.00}$ alloy was prepared by arc melting the mixture of pure metals (purity of 99.9 wt%) and then cut into small samples (25 ± 1 mg) to minimize the gravity effect. The high-purity W substrates with inevitable holes resulting from the powder metallurgy were mechanically ground and polished, whose surface roughnesses were measured by a surface profiler (Alpha-step IQ) to be about Ra5nm. The wetting experiments were performed using the modified sessile drop method. Differential scanning calorimetry (DSC, Netzsch 404C) analysis showed that the liquidus temperature of the alloy was 990 K. To ensure thermal and chemical stabilities, the droplet and W substrate were heated separately to 1173 K in vacuum of 5×10^{-4} Pa and held for 1 min, and then the droplet was dropped on the substrate and held for 30 min followed by furnace cooling.

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The whole process was monitored using an optical CCD camera. After the experiments, the samples were sectioned and polished for microstructural observation using a scanning electron microscope (SEM, FEI Quanta 600).

3. Results and discussion

3.1. Spreading kinetics under isothermal condition

Fig. 1 shows the real-time states, from which the drop base diameter and the drop height were measured and further the contact angle is calculated under the assumption of spherical cap approximation (Fig. 2(a)). The droplet spreads rapidly at the beginning and the contact angle stabilizes at about 29° when the driving force and the resistance are in balance. The small equilibrium contact angle and the fast spreading indicate that preparing composites using this alloy is feasible both thermodynamically and kinetically.

The forces controlling the drop spreading are studied here by fitting the spreading curve using the hydrodynamic model [12,13] and Jiang's empirical formula [14] (Fig. 2(b)). In the hydrodynamic model, the viscosity or viscous friction is the main resistance for the motion of the contact line, whereas Jiang's empirical formula does not have clear physical meaning. The hydrodynamic equation and the empirical formula can be written as Eq. (1) [15,16] and Eq. (2) [14], respectively:

$$\theta_d^3=\theta_e^3+9\frac{\mu v}{\gamma_{LV}}\ln(L/L_S) \tag{1}$$

$$\frac{\cos\theta_e-\cos\theta_d}{\cos\theta_e+1}=\tanh\left[4.96(\mu v/\gamma_{LV})^{0.702}\right] \tag{2}$$

where θ_d and θ_e are the dynamic and equilibrium contact angles, respectively, μ is the liquid viscosity, v is the spreading rate, $L=(2\gamma_{LV}/\rho g)^{1/2}$ (where γ_{LV} is the liquid surface tension, ρ is the liquid density and g is the gravitational acceleration) is the capillary length, and L_S is a cut-off height in the order of atomic or molecular dimension (10^{-9}–10^{-8} m). In this study, although the spreading time is much longer than that in the inert system [17], it is still not long enough to produce interfacial reaction. Fig. 3(b) also shows that the solid surface is flat and unbroken after the spreading, which agrees well with the assumption of the hydrodynamic model.

Both models describe the spreading behavior well. Therefore, it can be deduced that the drop spreading is mainly controlled by the viscosity. Besides, the fitting result of Jiang's empirical formula gives $\mu/\gamma_{LV}=0.329$ for this alloy, whose composition is close to $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1). The surface tension of Vit1 at 1173 K is about 1.47 N m^{-1} [18]. Substituting this value into the above result, it can be deduced that the viscosity here is about 0.48 Pa s, which is very close to the known experimental data [18,19]. The hydrodynamic equation gives $\mu/\gamma_{LV}\ln(L/L_S)=6.325$. Combining this result and taking $\rho=6.3\times10^3$ kg m^{-3} approximately, it can be deduced that $L_S=3\times10^{-11}$ m, which is less than the atomic dimension unreasonably [20–22]. This conflict indicates that some deviation exists using the hydrodynamic model. The main reasons may be that the viscous friction is not the only factor controlling the drop spreading and the hydrodynamic model simplifies the calculation under some assumptions [13]. For example, it ignores the difference of the substrate and assumes the solid surface is homogeneous chemically. Besides, it is pointed out that the slip length may not be constant with spreading rate [20].

3.2. Characteristics of the precursor film

Fig. 3(a) shows the macroscopic feature of the precursor film, whose thicknesses near the contact lines under different holding

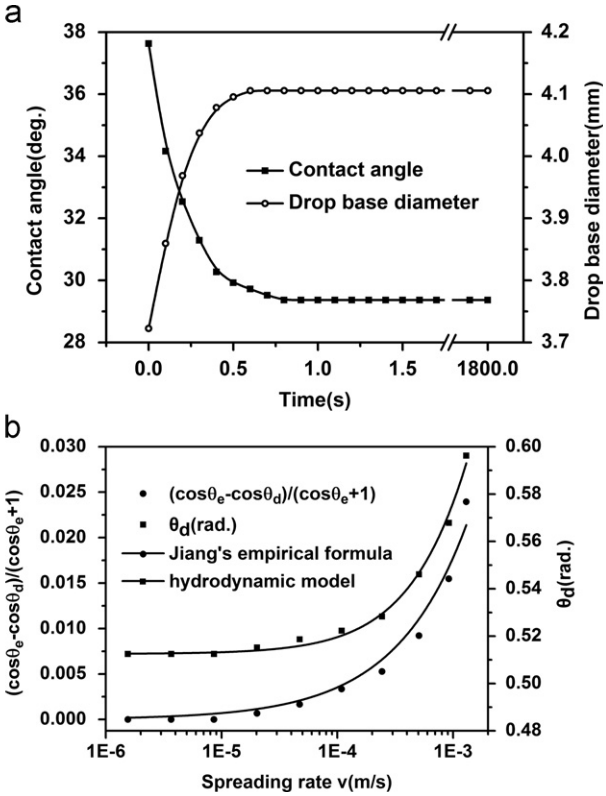

Fig. 2. (a) The dependence of contact angle and drop base diameter on time. (b) Fitting curves of the hydrodynamic model [12,13] and Jiang's empirical formula [14].

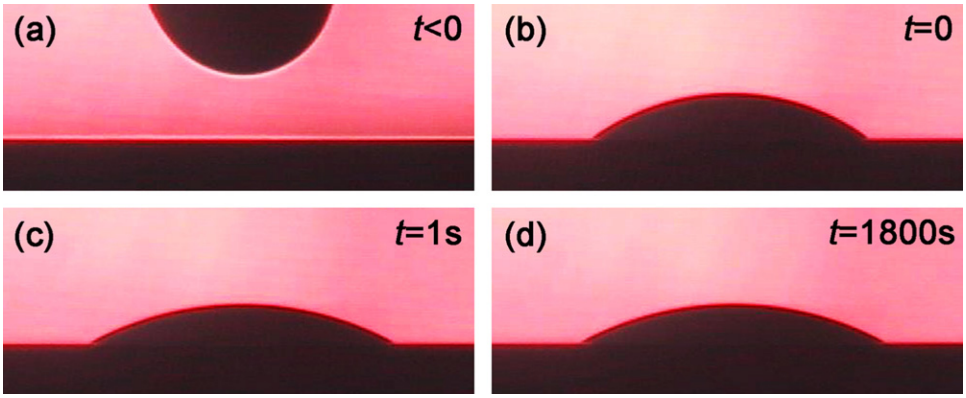

Fig. 1. The states of drop spreading at different times.