Wetting and coalescence of the liquid metal on the metal substrate*

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Molecular dynamics (MD) simulations are performed to investigate the wettability of liquid metal on the metal substrate. Results show that there exists different wettability on the different metal substrates, which is mainly determined by the interaction between the liquid and the substrate. The liquid metal is more likely to wet the same kind of metal substrate, which attracts the liquid metal to one side on the hybrid substrate. Exchanging the liquid metal and substrate metal has no effect on the wettability between these two metals. Moreover, the study of metal drop coalescing indicates that the metal substrate can significantly affect the coalescence behavior, in which the changeable wettability of liquid metal plays a predominant role. These studies demonstrate that the wetting behavior of liquid metal can be controlled by choosing the suitable metal substrate.

Keywords: molecular dynamics (MD) simulations, liquid metal, wettability, coalescence

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1. Introduction

Wettability, one of the most crucial physical properties to describe interfacial interaction between the liquid and the solid surface, has attracted extensive interest in recent years. The study of wettability may have a lot of practical applications in the fields of surface physics, surface chemistry, and material science.[1,2] Generally, wetting is a widely existing phenomenon in nature. For example, lotus leaves, as well as butterfly wings, display the self-cleaning effects which are related to the non-wetting of the surface,[3] this surface is also called the super-hydrophobic surface.[4] The advantage of amazing lotus leaf surface attracts people to study the reversible wettability from super-hydrophilic to super-hydrophobic[5] for certain purposes. By designing the antiwetting surface, the functions of anti-snow, anti-contamination and waterproof can be achieved in the advanced materials.[6,7] By adding the non-wetted coating, the anti-stick cookware is produced[8] for facilitating our daily life. On the other hand, enhancing the efficiency of pesticide spreading and mechanical lubrication needs good wetting of the surface, which makes the super-hydrophilic surface well studied simultaneously.[9–12] Like a water drop, the awareness of liquid metal wetting is even more meaningful because controlling the wettability of liquid metal not only determines the quality of materials in metallurgy and welding, but also provides strong possibilities to synthesize the highly desired composites.

Numerous theoretical or experimental studies have been performed to investigate the wettability of liquid metals.[13–21] Habenicht *et al.*[18] first reported that deformed Au films exposed to a pulsed laser could convert their surface deformation energy into kinetic energy, which makes them contract and finally jump from the substrate. The jumping droplet shows the dewetting properties on the non-wettable substrate. Then, Li *et al.*[13] studied the dewetting properties of the Cu film on nanopillared graphene, and demonstrated that the detachment can be controlled by tuning the geometrical parameters of the films and the surface nanostructures. The present study reveals the importance of the surface microstructure on the dewettability. It can be seen that much valuable work has been carried out to understand the wetting of liquid metal. However, existing studies mainly focus on the dewetting properties on the nonmetallic substrate, leaving the wettability between the metals poorly understood. The above studies show that the surface structure (also considered as the surface roughness) can greatly affect the wettability. But a large number of facts prove that the wettability remains different on the same smooth surface, manifesting that the underlying physical mechanisms of wetting are still under debate.

Due to the excellent characteristics, Al and its alloys, as the most well-known engineering materials, are widely used in electrical appliances, automobile components and aerospace components.[22–24] Studying the wettability of liquid Al is helpful. Additionally, Pb with the properties of corrosion-resistance and radiation-protection can be used to fabricate antiriot materials and shielding materials. In these materials, Pb always acts as the coating, which requires good wetting between the liquid Pb and the matrix. Therefore, understanding the wettability of liquid Pb with other metals plays an impor-

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tant role in fabricating these materials. Hence, in this work, we investigate the wettability of liquid Al and Pb on the different metal substrates and try to identify why the wettability is different. Moreover, the wettability of liquid Al–Pb alloy on the metal substrates is also explored. Previous studies[25,26] suggested that the substrate can affect the coalescence behavior by changing the wettability of drops. Given the variational wetting of liquid metal on the different metal substrates, it is reasonable to investigate the coalescence behavior of Al and Pb drops. These studies would give us an in-depth insight into the interfacial wetting phenomenon at an atomic level and provide the guidance in producing the new materials.

2. Models and simulation methods

The molecular dynamics (MD) simulations are performed to study the wettability of liquid Al, Pb, and Al–Pb alloy on the metal substrates. The MD simulations are carried out by using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package in the network virtual terminal *NVT* (where *N* refers to the number of atoms, *V* stands for volume, and *T* denotes temperature, which are all constant) ensemble. The temperature is held at 1500 K which is controlled by the Nose–Hoover thermostat,[27,28] and the velocity-verlet algorithm[29] is used to integrate the Newton's equation of motion in time steps of 1.0 fs. All the substrates are fixed in the simulation progress. Periodic boundary conditions are applied to the *x*, *y*, and *z* directions. The circular Al and Pb films each with a thickness of 15 Å and a radius of 54.12 Å, are obtained by melting the pure metal to 1500 K and relaxing for 500 ps. The Al–Pb alloys ($Al_{50}Pb_{50}$ is used in our simulations) are also melted to 1500 K and relaxed for 500 ps. Then, we place the Al films, Pb films and Al–Pb alloys on the different metal substrates to study the wettability for 600 ps, the coalescence processes of Al and Pb films on the metal substrates run 1500 ps. Al–Al, Pb–Pb, and Al–Pb interactions are described by an embedded atom method (EAM) potential,[30–32] which can be written as

$$E_i = F_\alpha\left(\sum_{j\neq i}\rho_\beta(r_{ij})\right) + \frac{1}{2}\sum_{j\neq i}\varphi_{\alpha\beta}(r_{ij}),$$

where *F* is the embedding energy, φ is a pair potential interaction. The empirical many-body potentials of Al–Pb system are constructed by using the "force matching" method. The potentials are fitted to experimental data and physical quantities, and are used for computer simulations of the thermodynamic properties of the Al–Pb system over a wide temperature range from 0 K to 2000 K, which can be validated by the computed Al–Pb phase diagram.[33] With the potentials, we calculate the equilibrium contact angles as 83.43° for Al and 112.12° for Pb on the flat graphene at 1500 K, which accord well with the experimentally measured contact angles of Al (about 85°)[34] and Pb (about 110°).[35]

3. Results and discussion

Figure 1 shows the wetting processes of the liquid Al on the four metal substrates. It can be seen that the wettability of liquid Al on the different substrates is quite different. On the Al and Pb sheets, the morphology of liquid Al only has a little change with time, indicating that the liquid Al can wet these two substrates in equilibration. But the wettability of liquid Al on the Al sheet is stronger than that on the Pb sheet. On the Mg sheet, the Al film gradually shrinks into a drop with time and finally detaches from the substrate, which displays the perfect non-wetting property. As mentioned in the Introduction, this behavior is also called dewetting. It is well known that the circular film can be converted into the hemisphere in shape due to the reduction of surface energy, reflected by the liquid Al shapes on the Al, Pb, and Mg substrates. However, the shape of liquid Al on the Fe sheet is drastically changed and fails to become spherical as shown in Fig. 1(d), which indicates that the effect of Fe sheet on the behavior of liquid Al is different from those of the previous three metals. To understand this behavior, we study the interaction between interfacial atoms. From the top view of the system in the *x*–*y* plane, it can be found that some Al atoms spread out on the Fe sheet and seem to form the stronger Al–Fe bonds. That is to say, the liquid Al and the Fe substrate produce the chemical reaction, and the wetting of liquid Al is on the AlFe compound substrate instead of the pure Fe substrate. As the simulation time increases, the spread area also enlarges. Therefore, it is hard for us to further investigate the wettability of liquid Al on the Fe substrate.

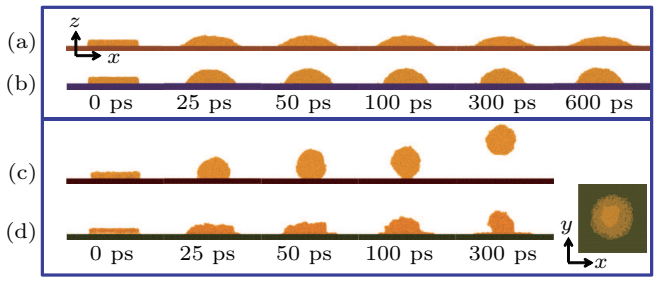


Fig. 1. (color online) The wetting processes of liquid Al on (a) Al sheet, (b) Pb sheet, (c) Mg sheet, and (d) Fe sheet. Yellow atoms indicate Al, other colors represent the different metal substrates, and the colors of liquid Al and sheets are unchanged in the following figures. The wetting behavior of liquid Al on the Fe sheet is abnormal, which is different from those of other substrates.

Contact angle is defined as the angle included between the substrate and the direction tangent to the particle surface starting from the triple point as shown in Fig. 2(a), which is predominantly used to characterize the surface wetting properties. To detailedly describe the wettability of liquid Al on the metals, we show the contact angles of liquid Al on the Al and Pb substrates in Fig. 2(b). On the Al substrate, the contact angle shows the decreasing tendency with time. On the Pb substrate, the contact angle first increases, then decreases, and

finally stays nearly unchanged after 400 ps. Why are the wetting behaviors of liquid Al different on these substrates? The average contact angles of liquid Al (from 400 ps to 600 ps) on the Al and Pb substrates are 20.33° and 47.05°, respectively, demonstrating that the liquid Al has the weak wettability on the Pb substrate. Due to the weak wettability on the Pb substrate, the liquid Al has to upheave with a fast speed to increase the contact angle at the beginning. After reaching equilibrium, the contact angle decreases and becomes relatively stable. According to the values of contact angles on the two substrates, we can conclude that the liquid metal is more likely to wet the same kind of metal substrate. Without the effect of the surface roughness, the reason for resulting in the different wettability may be related to the interaction between the liquid and the substrate. So we plot the curves of interaction energy versus time as shown in Fig. 2(c), it can be clearly seen that the Al–Al interaction energy is much larger than the Al–Pb interaction energy, which indicates that more Al atoms are in touch with the Al substrate and the Al–Al bonds are easy to form. The increasing of spread area of the liquid Al reduces the contact angle, thus leading to the good wettability. It is worth noting that the increasing tendency of the Al–Al interaction energy agrees well with the continuous decrease of contact angle. This is because all of them are related to the gradual enlargement of contact area driven by more Al atoms diffusing to the substrate surface. Additionally, the good lattice matching between the Al atoms also contributes to the good wettability.

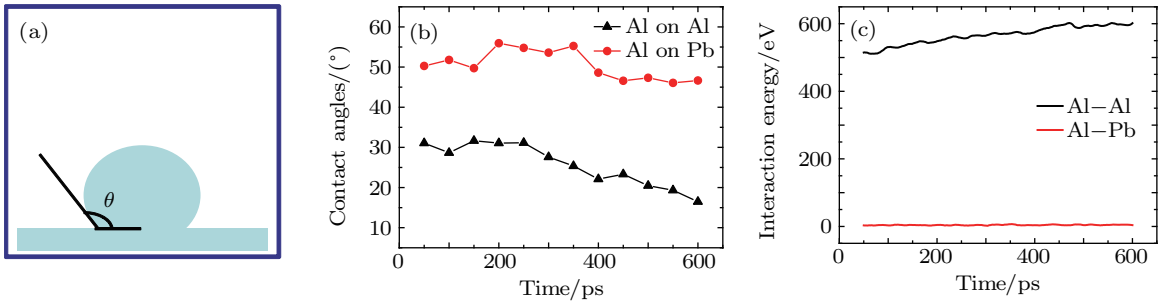


Fig. 2. (color online) (a) Definition of contact angle θ. (b) Comparison between contact angle of liquid Al on the Al substrate and that on Pb substrate. The contact angles of liquid Al on the Mg and Fe substrates are not presented in the graph because of the abnormal wetting behavior of liquid Al on the Fe substrate and the dewetting behavior on the Mg sheet. (c) Plots of interaction energy between the liquid Al and the substrates (Al–Al and Al–Pb) versus time, the interaction energy is actually a kind of potential energy.

Figure 3 shows the wettability of liquid Pb on the metal substrates. We mainly focus on the wettability of liquid Pb on the Al and Pb substrates in order to have a direct contrast with the liquid Al. In Figs. 3(a) and 3(b), it can be found that the wettability of liquid Pb on the Pb substrate is stronger than that on the Al substrate, which further proves the good wettability between the homogenous metals. As shown in Fig. 3(c), the average contact angles of liquid Pb (from 400 ps to 600 ps) on the Al and Pb substrates are 46.42° and 13.20°, respectively. It can be seen that the wettability of liquid Pb on the Al substrate (46.42°) is similar to that of liquid Al on the Pb substrate (47.05°), demonstrating that exchanging the liquid metal and the substrate metal have no obvious effects on the wettability between these two metals. Like liquid Al, the contact angle of liquid Pb shows the decreasing tendency on the Pb substrate, while it first increases and then decreases to a nearly unchanged value on the Al substrate. The interaction energy curve is also plotted in Fig. 3(c), and the larger Pb–Pb interaction energy is attributed to the good wettability on the Pb substrate.

The above discussion mainly focuses on the wettability of liquid metal on the single metal substrate. So what is the wetting behavior of liquid metal on the hybrid substrate? Figure 4(a) shows the wettability of liquid Al on the hybrid substrate that is composed of the Al sheet and the Pb sheet. Initially, the liquid Al is located in the centre of the substrate. As the simulation time increases, the liquid Al gradually moves to the Al sheet and totally stays on the Al sheet at 600 ps, the liquid Al just likes to be absorbed by the Al sheet because the wettability of Al on the Al substrate is wonderful. So if we place the liquid Pb on the hybrid substrate, it would move to the Pb side. To study the moving process, we display the center-of-mass displacement of liquid Al along the x direction. On the single Al metal substrate, the CMD_x curve is almost coincided with the dashed line, indicating that the liquid Al only has a little movement along the x direction. But on the hybrid substrate, the CMD_x curve declines and gradually keeps away from the dashed line, indicating that the liquid Al moves to the Al side. It can also be found that the moving speed of liquid Al changes from fast to slow, which may result from the change of interaction force. To illustrate the evolution of contact angles on the hybrid substrate by comparing with that on pure Al and pure Pb, we plot the variations of contact angles on the two sides with simulation time in Fig. 4(c). With the migrating of the droplet, the contact angle on the Al side increases, while it decreases on the Pb side. After 160 ps, the contact angles change a little, and the gap between these two contact angle curves becomes smaller. Compared with the contact angles

on pure Al and pure Pb, the contact angles on the Al side and Pb side are 39.93° and 42.43° (average values from 160 ps to 300 ps), respectively, which are larger than that on the pure Al substrate, but smaller than that on the pure Pb substrate. The contact angles of liquid Al on the hybrid substrate with the irregular alteration demonstrate that the wettability of liquid Al is significantly affected by the combination effect of the Al and the Pb sheets. After the liquid Al completely moves to the Al side, the contact angle is no longer affected by the Pb sheet. This finding may have the potential applications in separating the nanodroplet by designing the hybrid substrates.

Figure 5 shows the wetting processes of the liquid Al–Pb alloy on the metal substrate. As shown in Figs. 5(a) and 5(b), it can be seen that the shape evolutions of Al–Pb alloy and the distributions of Al and Pb atoms are quite different on these two substrates, which illustrates that the wettability of liquid Al–Pb alloy is different. Now, we come to ascertain how the metal substrate affects the wetting process of liquid Al–Pb alloy. Figure 5(c) shows the interfacial distributions of Al and Pb atoms. In the beginning, the distributions of Al and Pb atoms are disordered in the alloy. With the increase of simulation time, on the Al sheet, most of the Al atoms try to contact the substrate, and at the same time a small number of Pb atoms also diffuse into the substrate surface. The distributions of two atoms are relatively uniform. For the Pb sheet, it can be seen that the Al and Pb atoms are separated, most of the Pb atoms prefer to spread out on the substrate surface, and the Al atoms can also assemble together at the central position to touch the substrate. The different distribution of atoms makes the wettability different. We also give the contact angles of liquid Al–Pb alloy in Fig. 5(d), the average contact angles (from 300 ps to 600 ps) on the Al, Pb substrates are 25.52° and 18.44°. Therefore, the wettability of liquid Al–Pb alloy on the Al substrate is weaker than that on the Pb substrate. Interestingly, on the Al substrate, the contact angle of Al–Pb alloy is smaller than that of single Pb, but larger than that of single Al; on the Pb substrate, the contact angle of Al–Pb alloy is smaller than that of single Al, but larger than that of single Pb. Based on the above facts, the addition of some kinds of alloying elements which are beneficial to the wetting of the substrate can increase the wettability of liquid alloys.

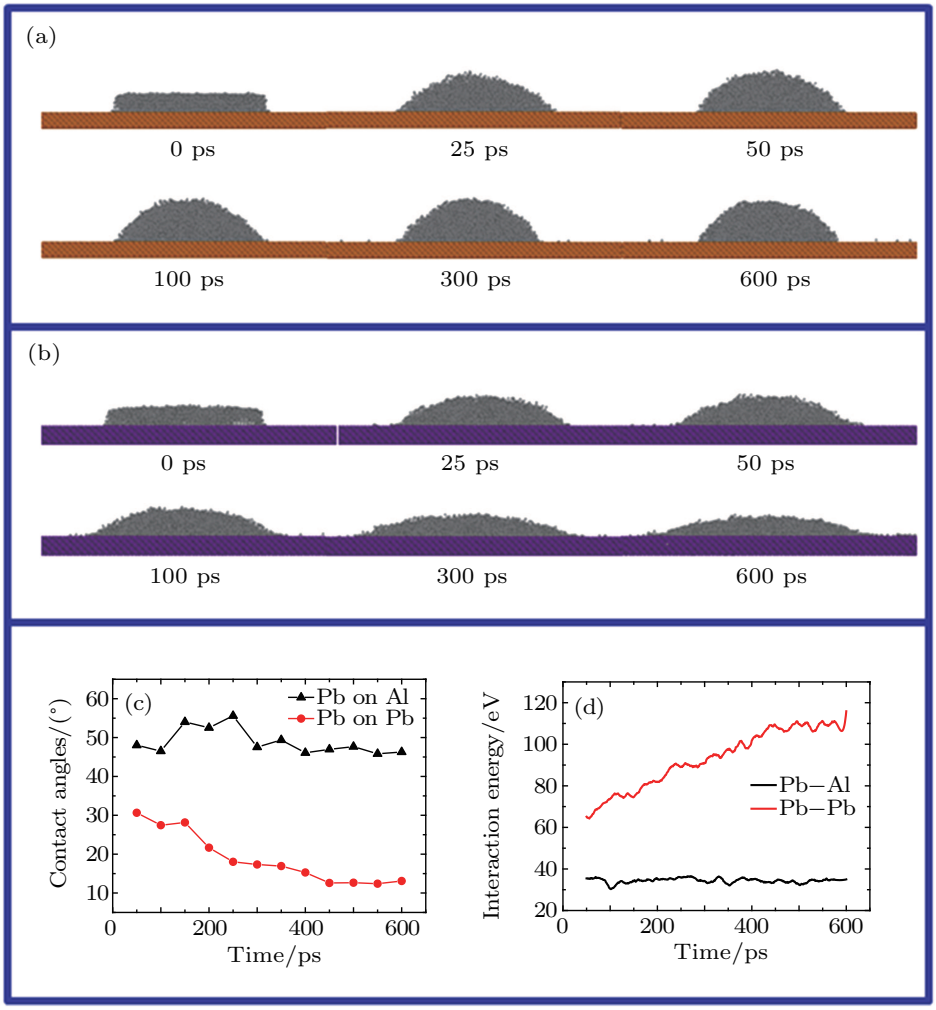


Fig. 3. (color online) Wetting processes of liquid Pb on (a) Al sheet and (b) Pb sheet. (c) Comparison between contact angles of liquid Pb on the Al and Pb substrates. (d) Variations of interaction energy between the liquid Pb and the substrates with time.

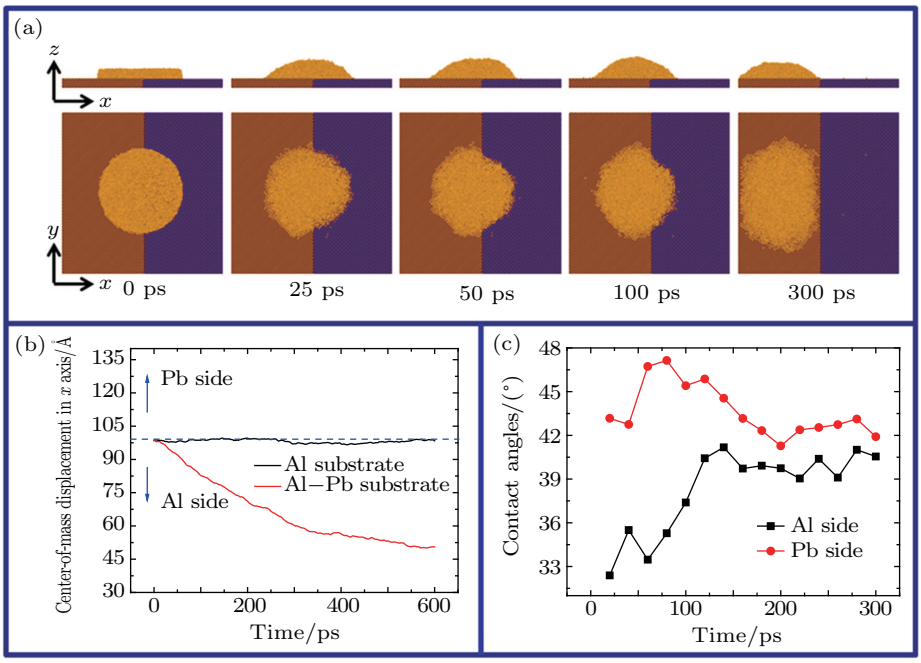


Fig. 4. (color online) Wettability of liquid Al on the hybrid substrate which is made up of the Al sheet (left) and Pb sheet (right). (a) Wetting process of liquid Al, the Al film is placed in the centre of the sheet. In the wetting process, the liquid Al ceaselessly moves along a certain direction, and after 600 ps, the liquid Al completely moves to the Al side. (b) Center-of-mass displacement of liquid Al along the x direction (CMD_x) on the Al substrate and hybrid Al–Pb substrate, the dashed line in the figure represents the central position of the substrates. (c) Contact angles of liquid Al on the Al side and Pb side before the liquid completely moves to the Al side.

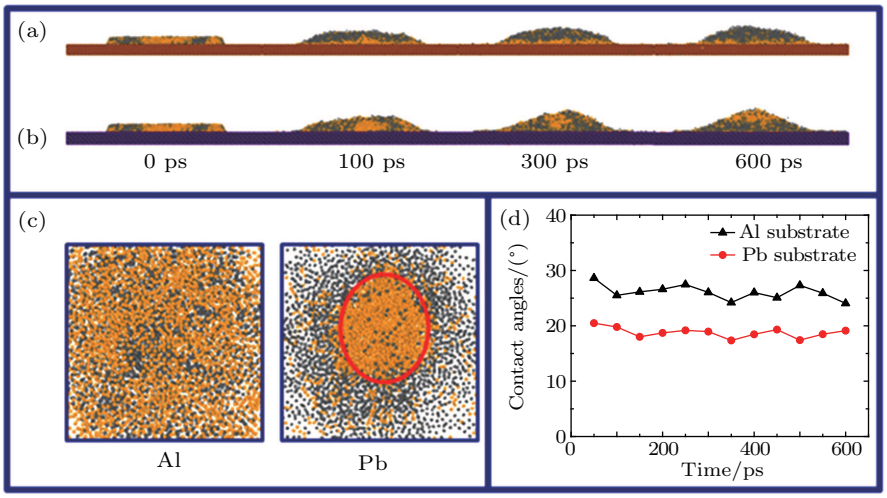


Fig. 5. (color online) Wettability of liquid Al–Pb alloy on (a) Al sheet and (b) Pb sheet. (c) Distributions of the Al and Pb atoms that are in contact with the substrates. (c) Comparison between contact angles of liquid Al–Pb alloy on the two substrates.

In order to know how the wettability affects the coalescence process, we also investigate the coalescence dynamics of liquid Al and Pb on the metal substrates as presented in Fig. 6(a). Initially, the Al and Pb films are adjacent to each other. As the simulation starts, two films begin to coalesce with a high speed and finally turn into one larger drop. However, the drop forming time is totally different on the two substrates. On the Al substrate, about 450 ps is needed to form one drop. On the Pb substrate, the coalescing time needs about 1200 ps, which is approximately three times longer than that on the Al substrate. The liquid wettability studied on the metal substrate can explain the difference in coalescing time. In the study of liquid Al–Pb alloy in Fig. 5, we can realize that the Pb atoms are above the Al atoms on the Al substrate, but for the Pb substrate, the Al atoms still contact the substrate and are not on the top of the Pb atoms. So in the coalescing process, the Pb atoms exhibit a strong upward motion to reside on the top and the Al atoms have good wetting on the Al substrate. The non-interference between two liquid metals is in favor of the coalescing process, leading to a short time for coalescence. On the Pb substrate, the Al atoms are not willing to reside above the Pb atoms, the Pb atoms also like to stick to the substrate due to the good wettability. This conflicting motion of two liquid metals obviously prolongs the coalescing time. In addi-

tion, it can be seen that the moving directions of the final drop are also different on the two substrates. The drop moves to the Al side on the Al substrate and moves to the Pb side on the Pb substrate. Center-of-mass displacements of the drop along the x and z directions are plotted to describe the drop movement. On the Al substrate, the CMD_x of Al descends and the CMD_x of Pb also has a large decrease, implying that the Al–Pb drop finally moves to the Al side after finishing the coalescing process. On the Pb substrate, the large rise of the Al–CMD_x curve and the nearly horizontal Pb-CMD_x curve indicate that the drop prefers to move to the Pb side. The different moving direction of the drop is also relevant to the wettability. For example, the liquid Al has a strong interaction with the Al substrate due to the good wettability, but the upheaval of liquid Pb which is evident on the Pb-CMD_z curve showing a weaker interaction with the Al substrate. In order to coalesce one drop, the Pb drop must move to the Al side to mix with the Al drop. Under the action of inertia force caused by the motion of Pb drop, the final coalesced drop moves along the negative direction of x-axis some distance, which is consistent with the decline of Al–CMD_x.

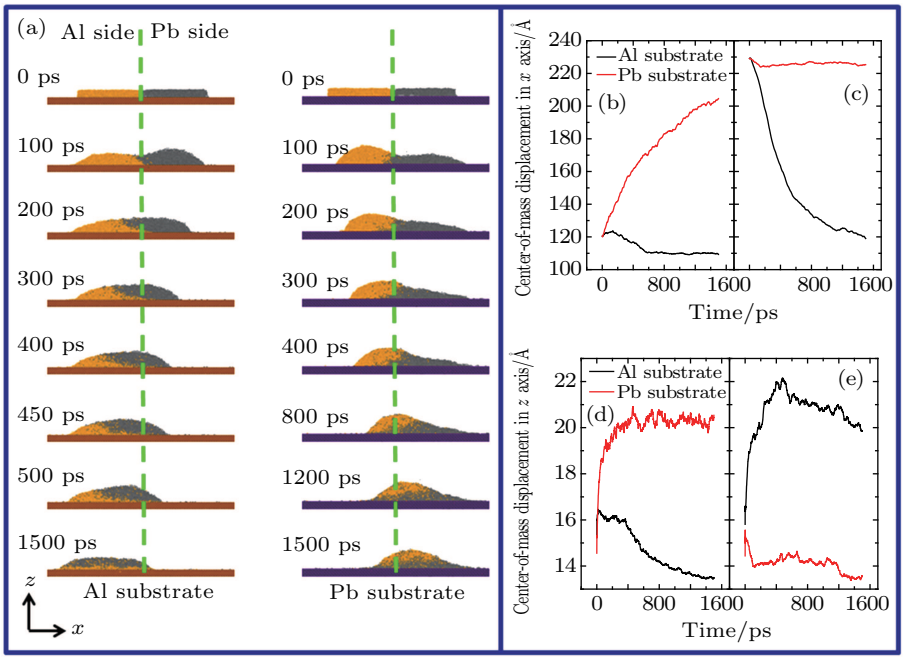


Fig. 6. (color online) Snapshots of coalescence dynamics and the center-of-mass displacement of metal drops. (a) Coalescence processes of the Al and Pb drops on the Al and Pb sheets, respectively. The green dashed line represents the initial boundary between the two metal films. Center-of-mass displacement of (b) Al and (c) Pb along the x direction (CMD_x), (d) Al and (e) Pb along the z direction (CMD_z) as a function of time. The changes of curves along the positive direction of x axis (the rise of curves) mean that the drop moves to the Pb side, and the change of curves along the negative direction (the fall of curves) indicates the Al side.

4. Conclusions and perspectives

In this work, the difference in wettability for the liquid Al on the different metals is great, the contact angles of liquid Al on the Al and Pb substrates are both smaller than 90°, but the Al drop can be detached from the Mg substrate to show the non-wetting properties. Comparison of the contact angles demonstrates that the liquid metal is more likely to wet the substrates with same chemical compositions, which drives the liquid metal to one side on the hybrid substrate. This finding may have the potential applications in separating the nanodroplet by designing the hybrid substrate. The wettability of liquid metal mainly depends on the interaction between the liquid and the substrate. So exchanging the liquid metal and the substrate metal has no obvious effect on the wettability between the two metals. The wettability of liquid Al–Pb alloy is better than that of single liquid metal on the heterogeneous substrate, implying that adding some kinds of metals which are beneficial to the wetting of the substrate can increase the wettability. Through affecting the wettability of single liquid metal, the metal substrates can significantly affect the coalescence behavior of metal drops.

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