

## Supporting information

### 1. Experimental Apparatus and Procedure

In a dispensed sessile drop method, the molten Al or Al-Si alloy (molten material) is deposited out of a dosing tube and then dropped directly onto the SiC substrate surface at the desired testing temperature. This method offers significant advantages such as: (i) mechanical removal of the initial surface oxide covering the molten material; (ii) ease of deciding the time when true wetting starts. (iii) minimization of the interaction between the substrate and molten material before the testing temperature is reached; and (iv) possibility of reducing the substrate surface contamination and stress by annealing the substrate at a higher temperature before the wetting initiation.

As can be seen from Fig. S-1, the apparatus has a double-layer stainless steel chamber with six-layer concentric Mo reflectors and a tantalum cylindrical heater, an evacuating system with a rotary pump and a turbo molecular pump (TMP), a gas purification pump, a temperature controlling system, a 10 mW He-Ne laser for illumination, a band-pass filter, a dispensed dropping device, a high-resolution ( $2000 \times 1312$  pixels) charge-coupled-device (CCD) camera with a remote controller, a video, an image automatic transmission and processing system. The TMP is located close to the chamber with a gate valve separating them such that a high vacuum can be achieved in a short time. The band-pass filter can cut all other wavelengths except for the laser beam (632 nm). As a result, the reflection light inside the chamber at high temperatures can be removed and high-definition drop profiles can be obtained.

After being ultrasonically cleaned, the SiC substrate is placed horizontally in the chamber while the molten material (Al cube, Al-Si cube) is placed in a glass cube with a spring connector on the top of the dropping device outside the chamber. The chamber is first evacuated to  $\sim 5 \times 10^{-4}$  Pa at room temperature, after that the temperature is first heated to 1373K, maintained for 10 min, and then cooled to the desired experimental temperature in vacuum (usually higher than  $5 \times 10^{-4}$  Pa before gas introduction). The gate valve (which isolates the chamber from the pumps) is then closed, and the purified Ar-3% H<sub>2</sub> gas is introduced to the chamber up to a pressure of  $\sim 120$  kPa ( $\sim 1.2$  atm). The oxygen partial pressure is estimated to be  $1.1 \times 10^{-4}$  Pa. After the temperature and the atmosphere have stabilized, both the gas inlet and outlet are closed, and the molten material is immediately inserted into the bottom of alumina dropping tube (99.6 wt.% purity) and kept for 1 minute for it to melt and reach the experimental temperature. The gas outlet is then slightly opened to let the pressure inside the chamber decrease to  $\sim 110$  kPa ( $\sim 1.1$  atm) and the molten material is forced out from a small hole ( $\phi=1$  mm) at the bottom of the alumina tube and dropped onto the SiC substrate.

Fig. S-2 shows the photographs recorded in this process. As soon as the molten material breaks away from the alumina tube, a photograph is taken and defined as the drop profile at zero time. Subsequent photographs are taken at certain time. After the wetting experiments, all drop photographs obtained by CCD camera are vector quantized by an axisymmetric drop shape analysis (ADSA) system to extract the data

points of the drop contour, which are then fitted and calculated through SESDROPD software to get the dynamic contact angles. After that the contact angle, the droplet diameter as well as the maximum height could be simultaneously calculated. ADSA is a powerful technique for the measurement of interfacial properties from the shape of drops. It relies on the best fit between theoretical curves and an experimental profile. The system consists of two parts. One is hardware, which consists of electronics, optical and mechanical components that generate a digital image of a drop. The other is software, which consists of image analysis and numerical schemes. This program offers a high degree of accuracy for calculation of the contact angle and essentially removes the operator's subjectivity. Despite the general success of ADSA, inconsistent results are obtained for drops close to spherical shape, which depends solely on the experimental profile and works accurately only for well-deformed drops.

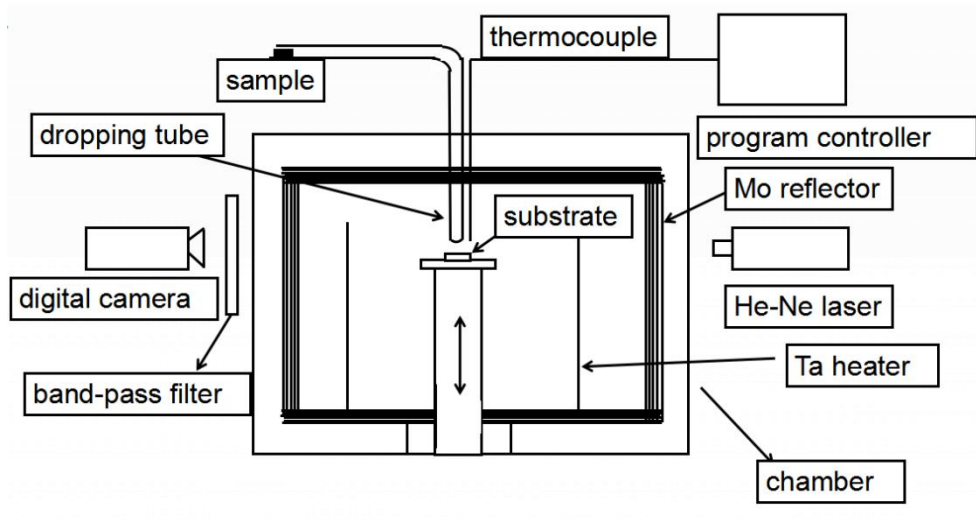


Fig. S-1 Schematic of experimental apparatus

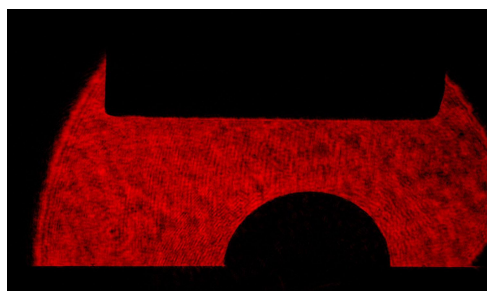


Fig. S-2 The drop photograph during the wetting experiment

## 2. Establishment of thermodynamics relations between three-phase tensions of reactive solid-liquid interfaces

The Young's equation is based on the equilibrium of the three-phase tension of wetting and the principle of a minimum free energy for the system, with the following

two conditions:

$$\sum \gamma_i = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cdot \cos \theta = 0 \quad (1)$$

$$\Delta G = 0 \quad (2)$$

where  $\Delta G$  is the free energy. Under these conditions, the Young's equation is given by:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos \theta \quad (3)$$

If the surface energy is denoted by  $\gamma_i$  and the surface tension is denoted by  $\vec{\gamma}_i$ , then  $(\vec{\gamma}_i \cdot \vec{r})$  is the resultant force along a certain direction, where  $r$  is the base radius of the liquid drop. As the solid-liquid surface tension  $\gamma_{sl}$  decreases during an interfacial reaction, the non-equilibrium three-phase tension and free energy of the wetting system are

$$\sum \gamma_i = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cdot \cos \theta \neq 0 \quad (4)$$

$$\Delta G \neq 0 \quad (5)$$

When the resultant force of the three-phase tension is non-zero, it becomes the driving force for the wetting and spreading of a liquid drop, leading to the decrease of contact angle  $\theta$ , the change in the free energy  $\Delta G$  caused by the spreading is the work  $\Delta w$  done by the driving force spreading the liquid drop over an increase area  $dA$ .

Suppose the radius of the solid-liquid interface is increased by  $dr$  of a consequence of reactive wetting, then the spreading area is increased by  $dA$  and  $\Delta w$  is given by:

$$\Delta w = \sum_0^{2\pi} \vec{\gamma}_i \cdot |\vec{r}| \cdot d\vec{r} = \sum_0^{2\pi} \frac{\vec{\gamma}_i \cdot \vec{r}}{|\vec{r}|} \cdot |\vec{r}| \cdot d\vec{r} \quad (6)$$

$$\Delta w = \sum_0^{2\pi} \frac{\vec{\gamma}_i \cdot \vec{r}}{|\vec{r}|} \cdot |\vec{r}| \cdot d|\vec{r}| = \sum_0^{2\pi} \gamma_i \cdot r \cdot dr$$

$$\Delta w = \sum_0^{2\pi} (\gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cos \theta) \cdot r \cdot dr$$

$$\Delta w = \int_0^{2\pi} (\gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cos \theta) \cdot r \cdot dr \cdot d\theta_L$$

$$\Delta w = 2\pi \cdot (\gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cos \theta) \cdot r \cdot dr$$

$$\Delta w = (\gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cos \theta) \cdot dA \quad (7)$$

In Eq. (7),  $\theta_L$  and  $\theta$  belong to different planes.  $\theta_L$  is the angle of the of the solid-liquid interface;  $\theta$  is the contact angle of the liquid drop perpendicular to the solid-liquid interface.

On the other hand, when the area of solid-liquid interface increases by  $dA$ , the overall change in free energy of the wetting system is  $\Delta G$ . This process satisfy the formula below:

$$\Delta G = -\gamma_{sv} \cdot dA + \gamma_{sl} \cdot dA + A \cdot d\gamma_{sl} + \gamma_{lv} \cdot dA \cdot \cos(\theta - d\theta) \neq 0 \quad (8)$$

The difference is that the solid-liquid interfacial tension  $\gamma_{sl}$  is treated as a constant in the Young's equation, while in Eq. (8)  $\gamma_{sl}$  is treated as a variable using a total differential computational method. In addition, when a dilute solution is used or when the change in the concentration of a liquid phase in an interfacial reaction can be neglected, then the volumetric free energy of the liquid remains constant at constant temperature and pressure. Therefore,  $\Delta G$  in Eq. (8) neglects the liquid volumetric free energy term.

In this reaction system, the change in systematic free energy  $\Delta G$  is achieved through work done by non-equilibrium force, thus the two following formula are obtained:

$$\Delta w = \Delta G \quad (9)$$

$$(\gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cos \theta) \cdot dA = -\gamma_{sv} \cdot dA + \gamma_{sl} \cdot dA + A \cdot d\gamma_{sl} + \gamma_{lv} \cdot dA \cdot \cos(\theta - d\theta) \quad (10)$$

From Eq. (10), it follows that:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos \theta + \frac{r}{4} \cdot \frac{d\gamma_{sl}}{dr} \quad (11)$$

Eq. (11) expresses the functional relationship among the surface tension, the liquid surface tension, and the solid-liquid interfacial tension of the reactive non-equilibrium wetting system. In form, Eq. (11) is a correction of the equilibrium Young's equation. When the solid-liquid interfacial tension  $\gamma_{sl}$  is stable, i.e.  $d\gamma_{sl}/dr = 0$ , the equilibrium Young's equation can be derived from Eq. (11). Thus Eq. (11) has universal significance, while the equilibrium Young's equation is a special case of the tension relationship in a reactive solid-liquid interface. As we can see from the differential term, Eq. (11) describes the mutual relationship among the tensions of the three phases at any time, and  $d\gamma_{sl}/dr \leq 0$  is allowed.

To clarify Eq. (11), further analysis is necessary. Suppose that the interfacial reaction layer is very thin (such as the wetting of an active brazing alloy on a ceramic surface), the volume of the liquid phase remains constant, and the influence of gravitational deformation is neglected, then the shape of the melting liquid drop is a spherical crown with radius of curvature  $R$  (Fig. S-3).

Thus when the shape of the liquid with constant volume changes, the functional relationship of the volume  $V$ , the radius of solid-liquid interface  $r$ , and the contact angle  $\theta$  becomes:

$$\begin{aligned} V &= \frac{\pi \cdot R^3}{3} \cdot (2 + \cos \theta) \cdot (1 - \cos \theta)^2 \\ &= \frac{\pi \cdot r^3 \cdot (2 + \cos \theta) \cdot (1 - \cos \theta)}{(1 + \cos \theta) \cdot \sin \theta} \end{aligned} \quad (12)$$

In the case where the change in liquid volume during the reaction process can be neglected, then:

$$dV = \frac{\partial V}{\partial r} + \frac{\partial V}{\partial \theta} = 0 \quad (13)$$

It follows that:

$$\frac{dr}{d\theta} = -\frac{r}{(2 + \cos \theta) \cdot \sin \theta} \quad (14)$$

When Eq. (14) is substituted into Eq. (11), then:

$$\gamma_{sv} - \gamma_{lv} \cdot \cos \theta = \gamma_{sl} - \frac{(2 + \cos \theta) \cdot \sin \theta}{4} \cdot \frac{d\gamma_{sl}}{d\theta} \quad (15)$$

When integration of Eq. (15) with the boundary condition  $\gamma_{sl}(\theta=180^\circ) = \gamma_{sv} + \gamma_{lv}$  is performed, the following is obtained:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos \theta - \gamma_{lv} \cdot \frac{(\cos^3 \theta + 4 \cos^2 \theta + \cos \theta - 6) + \sqrt[3]{16} \cdot (2 + \cos \theta)^{\frac{4}{3}} \cdot (1 - \cos \theta)^{\frac{4}{3}} \cdot (1 - \cos \theta)^{\frac{2}{3}}}{(1 + \cos \theta)^2} \quad (16)$$

Since:

$$f(\theta) = \frac{(\cos^3 \theta + 4 \cos^2 \theta + \cos \theta - 6) + \sqrt[3]{16} \cdot (2 + \cos \theta)^{\frac{4}{3}} \cdot (1 - \cos \theta)^{\frac{4}{3}} \cdot (1 - \cos \theta)^{\frac{2}{3}}}{(1 + \cos \theta)^2}$$

the following is obtained:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot [\cos \theta - f(\theta)] \quad (17)$$

Eq. (17) expresses the mathematical relationship of the solid surface tension, the liquid surface tension, and the solid-liquid interfacial tension at non-equilibrium in infinite solid-liquid interface. When compared with the equilibrium Young's equation

$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos \theta$ , the function  $f(\theta)$  appears as an extra term that is defined as the angle factor at non-equilibrium.

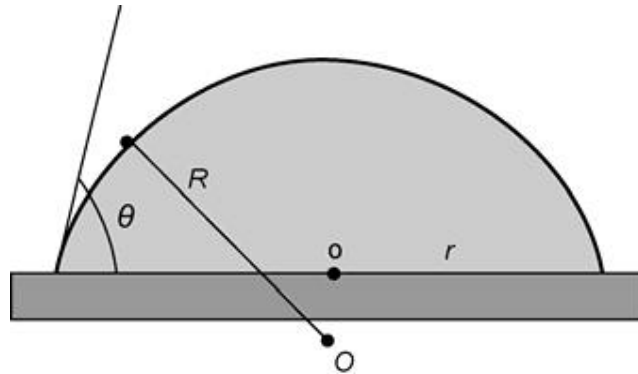


Fig. S-3 Schematic diagram of reactive wetting

### 3. Application of the wetting system for a characterized finite solid-liquid interface

Eq. (17) also has two unknowns,  $\gamma_{sv}$  and  $\gamma_{sl}$ , which cannot be solved directly. A limited solid-liquid wetting interface is used to correlate characterization and calculation; thus the unknowns can be solved by the establishment of two equations.

Fig. 1(a) shows the wetting of an infinite solid-liquid interface (a Young's equation system), and Fig. 1(b) shows the wetting of a finite solid-liquid interface designed for this study. Since the angle between Plane A and Plane B of the cylindrical infinite solid-liquid interface is  $90^\circ$ , two independent equations along the horizontal and vertical directions can be established, respectively. For wetting in the finite solid-liquid interface, the range of  $\theta_2$  at equilibrium is  $90^\circ \leq \theta_2 \leq 180^\circ$ .

As shown in Fig. 1(b), assume a liquid drop is located on a cylindrical finite solid surface, and it is at its initial state of reaction ( $\theta_2 \rightarrow \theta_{\max}$ , the theoretical maximum contact angle when gravitational pull is neglected and liquid loss is prevented). Furthermore, assume that the equilibrium of the three-phase tension is disturbed, and  $d\gamma_{sl}$  is the minor change of solid-liquid interfacial tension resulting from an interfacial reaction. Then the liquid will move along the direction of Plane B if the area of the solid-liquid interface remains unchanged. However, if the area of the solid-liquid interface is increased by  $dA$  (virtual displacement) and the contact angle  $\theta_2$  is decreased by  $d\theta$  (the volume of the liquid is constant), then transient equilibrium is maintained. In this case,  $\Delta G \neq 0$ . Thus the change in free energy of the finite solid-liquid wetting interface is expressed as

$$\Delta G = \gamma_{sl} \cdot dA + A \cdot \gamma_{sl} + \gamma_{lv} \cdot \cos(\theta_2 - d\theta) \neq 0 \quad (18)$$

Since the radius of the virtual finite solid-liquid interface is increased by  $dr$ , this change in energy is due to the work  $\Delta w$  done by the non-equilibrium force derived from the displacement  $dr$ . According to Fig. 1(b), the non-equilibrium resultant force along the direction of the finite solid-liquid interface is

$$\sum \vec{\gamma}_i = -\vec{\gamma}_{sl} - \vec{\gamma}_{lv} \cdot \cos \theta \neq 0 \quad (19)$$

When the area of the finite solid-liquid interface is increased by  $dA$ ,  $\Delta w$  done by this resultant force of three-phase tensions is

$$\Delta w = \sum_0^{2\pi} \vec{\gamma}_i \cdot |\vec{r}| \cdot d\vec{r} = \sum_0^{2\pi} \frac{\vec{\gamma}_i \cdot |\vec{r}|}{|\vec{r}|} \cdot |\vec{r}| \cdot d\vec{r} \quad (20)$$

$$\Delta w = (-\gamma_{sl} - \gamma_{lv} \cos \theta_2) \cdot dA \neq 0 \quad (21)$$

In this wetting system, the work done by the non-equilibrium force is equal to the change in free energy:

$$\Delta w = \Delta G \quad (22)$$

$$(-\gamma_{sl} - \gamma_{lv} \cdot \cos \theta_2) \cdot dA = \gamma_{sl} \cdot dA + A \cdot \gamma_{sl} + \gamma_{lv} \cdot \cos(\theta_2 - d\theta) \quad (23)$$

From Eq. (23), the following is derived:

$$\gamma_{sl} + \gamma_{lv} \cdot \cos \theta_2 + \frac{r}{4} \cdot \frac{d\gamma_{sl}}{dr} = 0 \quad (24)$$

When Eq. (24) is integrated and when  $\theta_2 \rightarrow 180^\circ$ , then  $\gamma_{sl}$  must be a finite value. Therefore, the integral constant  $C = \sqrt[3]{16} \cdot \gamma_{lv}$  is obtained, and hence

$$\gamma_{sl} = \gamma_{lv} \cdot \frac{2(\cos^2 \theta_2 - 3) + \sqrt[3]{16} \cdot (2 + \cos \theta_2)^{\frac{4}{3}} \cdot (1 - \cos \theta_2)^{\frac{2}{3}}}{(1 + \cos \theta_2)^2} \quad (25)$$

Eq. (25) is the functional relationship between the reactive solid-liquid interfacial tension obtained through the finite solid-liquid wetting interface  $\gamma_{sl}$  and the contact angle  $\theta_2$ . Eq. (25) demonstrates that the reactive solid-liquid interfacial tension  $\gamma_{sl}$  can be solved directly by measuring  $\theta_2$ .

According to Fig. 1(b), the surface tension of the solid  $\gamma_{sv}$  along the normal to the solid-liquid interface can be obtained as:

$$\gamma_{sv} = \gamma_{lv} \cdot \sin \theta_2 \quad (26)$$

This relation only applies to the initial state of reactive wetting. For a given solid substance, the numerical value in Eq. (27) has uniqueness.

Therefore, when  $\gamma_{sl}$  for the two systems is identical, the mathematical relation between  $\theta_1$  and  $\theta_2$  can be obtained by Eqs. (16, 17) and Eqs. (25, 26):

$$\cos \theta_1 - f(\theta_1) = \sin \theta_2 - \frac{2 \cdot (\cos^2 \theta_2 - 3) + \sqrt[3]{16} \cdot (2 + \cos \theta_2)^{\frac{4}{3}} \cdot (1 - \cos \theta_2)^{\frac{2}{3}}}{(1 + \cos \theta_2)^2} \quad (27)$$