

Theoretical analysis of reactive solid-liquid interfacial energies

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The characterization of reactive solid-liquid interfacial energies and solid surface energies is a pressing problem in materials science and surface science. Based on the concept that unbalanced forces doing work, a mathematical formulation between surface energies and interfacial energies for reactive wetting is presented. The resulting formalism has significant generality in which the equilibrium Young's equation for solid-liquid interfacial energies is just a special case. It is shown that a solid-liquid interfacial energy at non-equilibrium is always higher than that at equilibrium, and that the transformation of reactive interfaces to equilibrium interfaces is an inevitable, spontaneous process. The numerical range of solid-liquid interfacial energies γ_{sl} for a limited, solid-liquid interfacial wetting system was calculated to be $0 \leq \gamma_{sl} \leq \gamma_{sg}$. The calculation methods for reactive solid-liquid interfacial energies and solid surface energies are presented. They are significant for composite materials and weld, powder sinter, package of electronic devices, and other surface and interfacial issues in metallurgy.

reactive interface, solid-liquid interfacial energy, wettability, nonequilibrium, Young's equation, surface tension

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Welding, liquid-phase sintering, chemical reactions at solid surfaces in liquid media, metallurgy, and interfacial reactions and wetting phenomena of composite materials are examples of reactive solid-liquid interfacial processes. These interfaces are often important in materials preparation and processing. Because the solid-liquid interfacial energy γ_{sl} can change during interfacial reactions, its characterization has long been a challenge in surface and interface science. Since the Young's equation [1] was first proposed in 1805, the associated sessile drop method has been the most frequently applied method in the analysis of surface tension and solid-liquid interfacial energy. However, concerns arise as to whether the Young's equation is applicable to reactive solid-liquid interfaces. There has been no recognized model for the characterization of reactive interfaces. The Young's equation dictates that the numerical range of solid-liquid interfacial energies is $\gamma_{sg} - \gamma_{lg} \leq \gamma_{sl} \leq \gamma_{sg} + \gamma_{lg}$, where γ_{sg} is the solid surface energy and γ_{lg} is the liquid surface energy. However, two problems arise: (1) Is $\gamma_{sl} \rightarrow 0$ tenable when the

contact angle $\theta \rightarrow 0$? In other words, is there a situation where $\gamma_{sg} = \gamma_{lg}$ is true? (2) When θ is greater than 90° or when $\theta \rightarrow 180^\circ$, why is the solid-liquid interfacial energy calculated from the Young's equation greater than either the liquid or solid surface energies? These problems emerge from the Young's equation because there is only one equation along the direction of the solid-liquid interface for an infinite solid-liquid wetting system, and thus the internal relation between γ_{sg} and γ_{sl} is undetermined and the selection of these two values has a certain randomness. Extensive research has been conducted on the wetting of non-active interfaces [2–5], and the conclusion has been that the theoretical condition for complete wetting of a liquid on a solid surface is $\gamma_{sg} = \gamma_{lg}$ [6–8]. For the wetting of a finite solid-liquid interface, we have proved that when $\theta \rightarrow 0$, the theoretical conditions for the complete wetting of a liquid on a solid surface is $\gamma_{sl} \rightarrow 0$ and $\gamma_{sg} = \gamma_{lg}$ [9,10]. The experimental data for the surface energy of five ceramics [11] and six polymers [12] were consistent with calculations; and the hydrophobicity of lotus leaves was explained by the limited solid-liquid interfacial wettability [13]. However, there is no

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rigorous and widely accepted theoretical model for the three-phase tension of reactive wetting interfaces. There have been many experimental only studies results of reactive wetting [14–16]. For example, Yost and Romig [17] suggested that the driving force consists of two parts:

$$\frac{1}{2\pi r} \cdot \frac{dE}{dr} = \Delta G_f + \Gamma(\theta),$$

where E is the free energy of the system, ΔG_f is the driving force for the formation of a new phase at the solid-liquid interface, $\Gamma(\theta)$ is the driving force for the tension at the non-equilibrium interface, and r is the base radius of the liquid drop. The energy released by chemical and physical changes at the interface is the major driving force for reactive wetting.

If the contact angle of the reaction interface at non-equilibrium is θ_d and the contact angle at equilibrium is θ_{eq} , Attar and Korner [18] have shown that the resulting unbalanced force F_x that facilitates the transformation from $\theta_d \rightarrow \theta_{eq}$ is given by

$$F_x = \gamma_{sg} - \gamma_{sl} - \gamma_{lg} \cdot \cos \theta_d \\ = -\frac{3}{2r} \cdot \gamma_{lg} \cdot (\theta_{eq} - \theta_d) \cdot \sin\left(\frac{\theta_{eq} + \theta_d}{2}\right).$$

Here, r is the base radius of the liquid drop and F_x is a function of the difference in contact angle before and after interfacial reaction.

In their studies of reactive wetting, Attard [19] and Kolev et al. [20] considered a time-dependent tension of the reactive solid-liquid interface, with a modified Young's equation:

$$\gamma_{os} = \gamma_{ws} + \gamma_{ow} \cos \theta + \gamma_d.$$

Here the corrected term $\gamma_d = -\beta \cdot d\gamma_c/dt$, β is the undetermined coefficient of linear resistance, and the corrected term γ_d and the solid-liquid interface are time-dependent. The Young's equation is essentially a time-independent thermodynamic energy relation between surface and interface tensions. Meanwhile, the reaction dynamics is greatly affected by reaction temperature. Yan et al. [21] and Protsenko et al. [22] proposed a double-spherical-crown model for the liquid on both sides of a wetting interface. By assuming the formation of a very thin layer of small spherical crowns on the solid side following the solid-liquid interfacial reaction, the model is consistent with the Young's equation. Yan et al. [21] proposed a factor λ for the characterization of wetting at the reactive solid-liquid interface. Using this factor, the difference of the liquid-solid phase interfacial tension and the liquid-gas phase interfacial tension [$\Delta\sigma(\Delta\sigma = \sigma_{ls} - \sigma_{lg})$] and the work of adhesion were calculated. However, this model, under the premise that the volume of the liquid phase remains constant, neglects the increase in the area of the solid-liquid interface during spreading and the decrease in contact angle during the reac-

tion process. Fukuda et al. [23], starting with the double-spherical-crown model and taking account of the fact that the solid-phase dissolves violently during the wetting of Cu-B/Cu and Ag-Bi/Ag interfaces, used equation

$$\left[\frac{\sigma_{SL}}{\sin \theta_v} = \frac{\sigma_L}{\sin \theta_s} = \frac{\sigma_s}{\sin(\theta_1 + \theta_2)} \right]$$

for the calculation of the surface tension for the solid and liquid at equilibrium. The calculation was conducted by measuring the angles among the solid, liquid and gas phases at room temperature, and the resulting σ_{SL} values were only for the interface reaction at equilibrium. However, for the situation where interfacial dissolution is obscured ($\theta_s \rightarrow 180^\circ$), no solution can be calculated with this equation due to non-equilibrium forces.

Laurent et al. [24] introduced negative free energy into the Young's equation. For wetting of an active filler metal for brazing ceramics, the equation for the minimum contact angle is

$$\cos \theta_{\min} = \cos \theta_0 - \frac{\Delta\delta_r}{\delta_{lv}} - \frac{\Delta G_f}{\delta_{lv}}.$$

However, it is difficult to determine which term for the contact angle is dominant in active wetting.

Thus the calculation of reactive solid-liquid interfacial energies is still an unsolved problem. The work presented here attempts to provide a rigorous theoretical basis for a solution.

1 Establishment of thermodynamic relations among 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:

$$\sum \vec{\gamma}_i = \vec{\gamma}_{sg} - \vec{\gamma}_{sl} - \vec{\gamma}_{lg} \cdot \cos \theta = 0, \quad (1)$$

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

Under these conditions, the Young's equation is given by

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cdot \cos \theta. \quad (3)$$

If the surface energy is denoted by γ_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.

As the solid-liquid surface energy γ_{sl} decreases during an interfacial reaction, the non-equilibrium three-phase tension and free energy of the wetting system are

$$\sum \vec{\gamma}_i = \vec{\gamma}_{sg} - \vec{\gamma}_{sl} - \vec{\gamma}_{lg} \cdot \cos \theta \neq 0, \quad (4)$$

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

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 θ . The change in free energy ΔG caused by the spreading is the work Δw done by the driving force spreading the liquid drop over an increased area dA .

Suppose the radius of the solid-liquid interface is increased by dr as a consequence of reactive wetting, then the spreading area is increased by dA and Δw is given by

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

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

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

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

$$\Delta w = 2\pi \cdot (\gamma_{sg} - \gamma_{sl} - \gamma_{lg} \cos \theta) \cdot r \cdot dr,$$

$$\Delta w = (\gamma_{sg} - \gamma_{sl} - \gamma_{lg} \cos \theta) \cdot dA. \quad (7)$$

In eq. (7), θ_L and θ belong to different planes. θ_L is the angle of the plane of the solid-liquid interface; θ is the contact angle of the liquid drop perpendicular to the solid-liquid interface.

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

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

The difference is that the solid-liquid interfacial energy γ_{sl} is treated as a constant in the Young's equation, while in eq. (8) γ_{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, ΔG in eq. (8) neglects the liquid volumetric free energy term.

In this reaction system, the change in systematic free energy ΔG is achieved through work done by the non-equilibrium force, thus the following two formulas are obtained:

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

$$(\gamma_{sg} - \gamma_{sl} - \gamma_{lg} \cdot \cos \theta) \cdot dA = -\gamma_{sg} \cdot dA + \gamma_{sl} \cdot dA + A \cdot d\gamma_{sl} + \gamma_{lg} \cdot dA \cdot \cos(\theta - d\theta). \quad (10)$$

From eq. (10), it follows that

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

Eq. (11) expresses the functional relationship among the solid surface energy (surface tension), the liquid surface energy (interface tension), and the solid-liquid interfacial energy (surface 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 energy γ_{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 energy relationship in a reactive solid-liquid interface. As we can see from the differential term, eq. (11) describes the mutual relationship among the energies 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 (Figure 1).

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 θ becomes

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

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

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

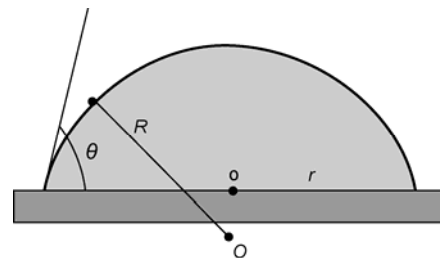


Figure 1 Schematic diagram of reactive wetting.

When eq. (14) is substituted into eq. (11), then

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

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

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

Since

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

the following is obtained:

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cdot [\cos \theta - f(\theta)]. \quad (17)$$

Eq. (17) expresses the mathematical relationship of the solid surface energy, the liquid surface energy, and the solid-liquid interfacial energy at non-equilibrium. When compared with the equilibrium Young's equation $\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cdot \cos \theta$, the function $f(\theta)$ appears as an extra term that is defined as the angle factor at non-equilibrium.

When the contact angle θ is identical, through the difference between eq. (17) and the Young's equation, the difference $\Delta\gamma_{sl}$ of the solid-liquid interfacial energy before and after interfacial reaction (i.e. at equilibrium and non-equilibrium) can be obtained as

$$\Delta\gamma_{sl} = \gamma_{lg} \cdot f(\theta); \quad f(\theta) = \frac{\Delta\gamma_{sl}}{\gamma_{lg}}. \quad (18)$$

Figure 2 shows the relationship between the angle factor $f(\theta)$ and the contact angle θ at non-equilibrium, which also

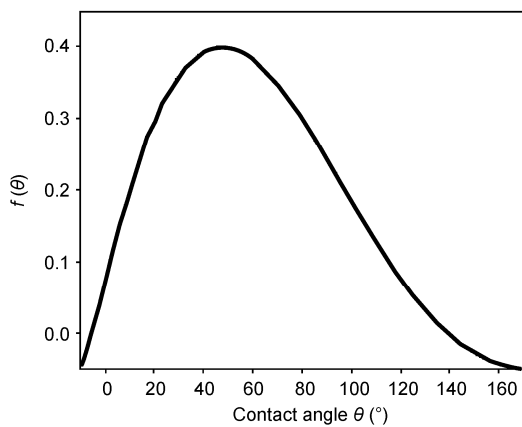


Figure 2 Relationship between angle factor and contact angle at non-equilibrium.

represents the difference in values between the solid-liquid interfacial energies at non-equilibrium and those at equilibrium. It also can be seen that the solid-liquid interfacial energy at non-equilibrium is always higher than that at equilibrium. Figure 2 reveals that the non-equilibrium interface is a thermodynamically unstable state. The loss of energy through interfacial reaction is an inevitable and spontaneous process.

When $\theta=57.36^\circ$, $f(\theta)$ is maximized, indicating that at this contact angle, the difference between the reactive interfacial energy and the equilibrium interfacial energy reaches its maximum. When θ is 0° or 180° , there is no difference because when $\theta = 0^\circ$, the liquid is perfectly wet on the solid surface, and the solid-liquid interfacial energies at both equilibrium and non-equilibrium are zero. When $\theta = 180^\circ$, the solid-liquid interfacial reaction does not occur, indicating that the interface is at equilibrium.

2 Application of the wetting system for a characterized finite solid-liquid interface

Eq. (17) also has two unknowns, γ_{sg} and γ_{sl} , which cannot be solved directly. In this study, 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.

Figure 3 shows the wetting of an infinite solid-liquid interface (a Young's equation system), and Figure 4 shows the wetting of a finite solid-liquid interface designed for this study [9,10]. Since the angle between Plane A and Plane B of the cylindrical infinite solid-liquid interface is 90° , two independent equations along the horizontal and vertical directions can be established, respectively. For wetting in the finite solid-liquid interface, the range of θ_2 at equilibrium is $90^\circ \leq \theta_2 \leq 180^\circ$ [9].

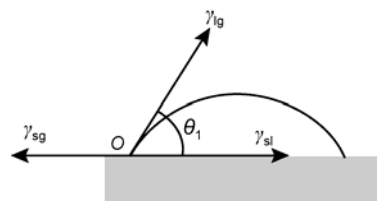


Figure 3 Distribution of tension in an infinite solid-liquid interface.

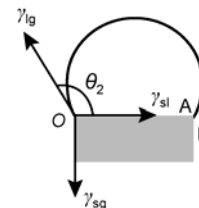


Figure 4 Distribution of tension in a finite solid-liquid interface.

As shown in Figure 4, 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 energy 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 θ_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

$$\Delta G = \gamma_{sl} \cdot dA + A \cdot d\gamma_{sl} + \gamma_{lg} \cdot \cos(\theta_2 - d\theta) \neq 0. \quad (19)$$

Since the radius of the virtual finite solid-liquid interface is increased by dr , this change in energy is due to the work Δw done by the non-equilibrium force derived from the displacement dr . According to Figure 4, the non-equilibrium resultant force along the direction of the finite solid-liquid interface is

$$\sum \vec{\gamma}_i = -\vec{\gamma}_{sl} - \vec{\gamma}_{lg} \cdot \cos \theta \neq 0. \quad (20)$$

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

$$\Delta w = \sum_0^{2\pi} \vec{\gamma}_i \cdot |\vec{r}| \cdot d\vec{r} = \sum_0^{2\pi} \frac{\vec{\gamma}_i \cdot |\vec{r}|}{|\vec{r}|} \cdot |\vec{r}| \cdot d\vec{r}, \quad (21)$$

$$\Delta w = (-\gamma_{sl} - \gamma_{lg} \cdot \cos \theta_2) \cdot dA \neq 0. \quad (22)$$

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

$$\Delta w = \Delta G, \quad (23)$$

$$(-\gamma_{sl} - \gamma_{lg} \cdot \cos \theta_2) \cdot dA = \gamma_{sl} \cdot dA + A \cdot d\gamma_{sl} + \gamma_{lg} \cdot dA \cdot \cos(\theta_2 - d\theta). \quad (24)$$

From eq. (24), the following is derived:

$$\gamma_{sl} + \gamma_{lg} \cdot \cos \theta_2 + \frac{r}{4} \cdot \frac{d\gamma_{sl}}{dr} = 0. \quad (25)$$

When eq. (25) is integrated and when $\theta_2 \rightarrow 180^\circ$, then γ_{sl} must be a finite value. Therefore, the integral constant $C = \sqrt[3]{16} \cdot \gamma_{lg}$ is obtained, and hence

$$\gamma_{sl} = \gamma_{lg} \cdot \frac{2(\cos^2 \theta_2 - 3) + \sqrt[3]{16} \cdot (2 + \cos \theta_2)^4 \cdot (1 - \cos \theta_2)^2}{(1 + \cos \theta_2)^2}. \quad (26)$$

Eq. (26) is the functional relationship between the reactive solid-liquid interfacial energy obtained through the finite solid-liquid wetting interface γ_{sl} and the contact angle θ_2 . Eq. (26) demonstrates that the reactive solid-liquid interfacial energy γ_{sl} can be solved directly by measuring θ_2 .

According to Figure 4, the surface energy of the solid γ_{sg} along the normal to the solid-liquid interface can be obtained as [9]:

$$\gamma_{sg} = \gamma_{lg} \cdot \sin \theta_2. \quad (27)$$

This relation only applies to the initial state of reactive wetting. For a given solid substance, the numerical value in eq. (27) has uniqueness. In the case of an interface reaction where a minor increase in dr and $d\theta$ occurs, the following formula [9] is still applicable under extreme conditions:

$$\gamma_{sg} = \gamma_{lg} \cdot \sin(\theta_2 - d\theta) \rightarrow \gamma_{lg} \cdot \sin \theta_2.$$

3 Numerical range of the solid-liquid interfacial energy

Figure 5 depicts the functional relationship between the solid surface energy γ_{sg} and the contact angle θ_2 , derived from eq. (27), $0 \leq \gamma_{sg} < \gamma_{lg}$, $90^\circ < \theta_2 \leq 180^\circ$.

Figure 5 indicates that the surface energy of the solid will not be greater than that of the liquid, and that the theoretical boundary condition for the complete wetting of the liquid phase on the surface of solid phase is $\gamma_{sg} = \gamma_{lg}$. The analysis of the contact angle makes sense only when $\gamma_{sg} \leq \gamma_{lg}$. For a completely non-wetting state, $\gamma_{sg} \rightarrow 0$. Actually, the surface energy of any solid will be non-zero. When it is very small compared with that of the liquid ($\gamma_{sg}/\gamma_{lg} \rightarrow 0$), complete non-wetting state will take place.

Figure 6 displays the functional relationship between the reactive solid-liquid interfacial energy γ_{sl} , and the contact

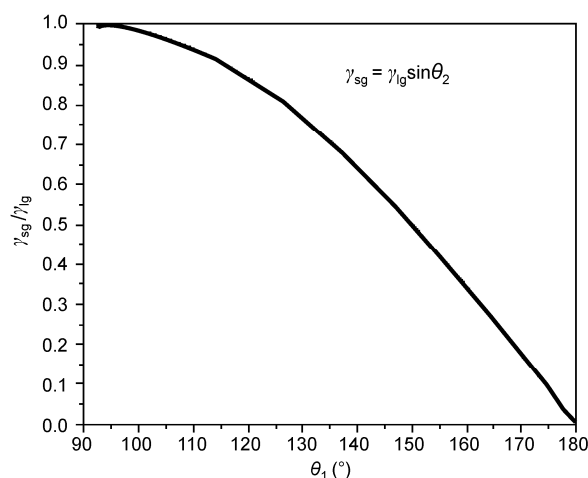


Figure 5 Relationship between the solid surface energy γ_{sg} and the contact angle θ_2 at the finite solid-liquid interface.

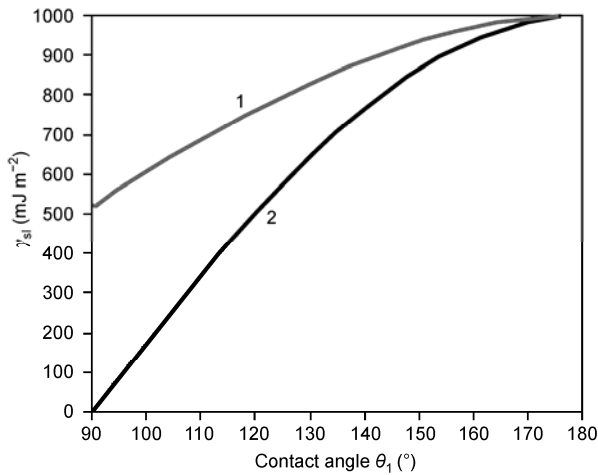


Figure 6 Relation between the solid-liquid interfacial energy and the contact angle at the finite solid-liquid interface.

angle θ_2 obtained through the wetting system of the finite solid-liquid interface. In this figure, the surface energy of a given liquid metal is set to 1000 mJ m^{-2} . Curve 1 is the non-equilibrium state according to eq. (26); curve 2 is the equilibrium state [9] of the finite solid-liquid interface, and its expression is given as

$$\gamma_{sl} = -\gamma_{lg} \cdot \cos \theta_2, 90^\circ \leq \theta_2 \leq 180^\circ. \quad (28)$$

Figure 6 indicates that when $\theta_2 \rightarrow 180^\circ$, $\gamma_{sl} \rightarrow \gamma_{lg}$, which is consistent with the result derived from the non-reactive finite solid-liquid interface [9,10]. The maximum value obtained for the solid-liquid interfacial energy is given by $(\gamma_{sl})_{\max} \rightarrow \gamma_{lg}$. This result proves that γ_{sl} of any wetting system will not exceed the liquid surface energy γ_{lg} (the maximum). This also indicates that the solid surface energy in a non-wetting state is very small compared with that of the liquid. The reason is that no matter how much a material with high surface energy absorbs liquid, its original surface energy will always decrease. That is, the newly formed solid-liquid interfacial energy is less than the solid surface energy. Similarly, if a liquid drop of high surface energy contacts a solid of lower surface energy, the liquid-phase surface energy will decrease as long as the wetting state exists. Even if the wetting is poor, the solid-liquid interfacial energy will not be larger than the surface energy of the largest phase of the whole system as long as there is a certain amount of wetting ($90^\circ < \theta \leq 180^\circ$). The empirical state equation [25] $\gamma_{sl} = \gamma_s + \gamma_l - 2\phi\sqrt{\gamma_s \cdot \gamma_l}$ derived by Good-Girifalco can be combined with the Young's equation to obtain [10]:

$$\gamma_{sl} = \gamma_{lg} \cdot \left[\frac{(1 + \cos \theta)^2}{4\phi^2} - \cos \theta \right],$$

from which we can see that no matter what the value of ϕ is, $(\gamma_{sl})_{\max} \rightarrow \gamma_{lg}$.

Young-Good-Girifalco's equation also indicates that γ_{sl} will not be larger than γ_{sg} . Since it is empirical (the value of ϕ needs to be confirmed by experiment), it is not a theoretical demonstration in the strict sense. Figure 6 demonstrates that the solid-liquid interfacial energy at non-equilibrium is always higher than that at equilibrium, which further indicates that the reactive interface at non-equilibrium is thermodynamically instable, and the reduction of energy via interface reaction is an inevitable, spontaneous process. When $\theta_2 \rightarrow 90^\circ$, the non-reactive solid-liquid interfacial energy is zero, while the reactive solid-liquid interfacial energy is still greater than zero. This is because curve 1 is a thermodynamically non-equilibrium relation and the corresponding interface reaction is still in a transition state.

4 An efficient computational method for the reactive solid-liquid interfacial energy

Although the reactive solid-liquid interfacial energy and the solid surface energy can be determined by measuring the contact angle θ_2 , it is experimentally difficult to obtain the maximum value of θ_2 . However, the measurement of the contact angle θ_1 of the infinite solid-liquid interface is feasible. Therefore, the mathematical relation between θ_1 and θ_2 must be derived.

Three reactive wetting equations for two different wetting systems have been obtained as

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cdot [\cos \theta_1 - f(\theta_1)], \quad 0^\circ \leq \theta_1 \leq 180^\circ, \quad (29)$$

$$\gamma_{sg} = \gamma_{lg} \cdot \sin \theta_2, \quad 90^\circ \leq \theta_2 \leq 180^\circ, \quad (30)$$

$$\gamma_{sl} = \gamma_{lg} \cdot \frac{2 \cdot (\cos^2 \theta_2 - 3) + \sqrt[3]{16} \cdot (2 + \cos \theta_2)^4 \cdot (1 - \cos \theta_2)^2}{(1 + \cos \theta_2)^2}, \quad 90^\circ \leq \theta_2 \leq 180^\circ. \quad (31)$$

The surface energies of the solid and the liquid in the two wetting systems of infinite and finite solid-liquid interfaces are constant. Therefore, when γ_{sl} for the two systems is identical, these three equations can be used to obtain the mathematical relation between θ_1 and θ_2 :

$$\cos \theta_1 - f(\theta_1) = \sin \theta_2 \cdot \frac{2 \cdot (\cos^2 \theta_2 - 3) + \sqrt[3]{16} \cdot (2 + \cos \theta_2)^4 \cdot (1 - \cos \theta_2)^2}{(1 + \cos \theta_2)^2}. \quad (32)$$

Figure 7 shows the functional relationship between $\cos \theta_1$ and $\cos \theta_2$.

Therefore, γ_{sl} , the solid-liquid interfacial energy at the initial state of reaction, and γ_{sg} , the solid surface energy, can be calculated according to the following procedure. The

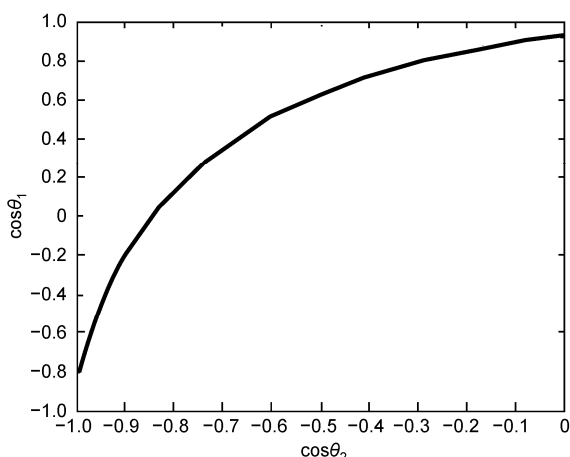


Figure 7 Functional relation between $\cos\theta_1$ and $\cos\theta_2$.

initial-state contact angle θ_1 of the wetting system of infinite solid-liquid interface is first measured by experiment; then θ_2 is calculated by eq. (32) or Figure 7. Finally, θ_2 is substituted into eqs. (26) and (27). It should be noted that θ_2 represents the initial-state contact angle, and therefore the corresponding θ_1 and γ_{sl} are also initial values. Since γ_{sg} remains unchanged, the solid-liquid interfacial energy γ_{slF} at the final equilibrium state can be solved by the Young's equation $\gamma_{slF} = \gamma_{sg} - \gamma_{lg} \cdot \cos\theta_{1F}$, once the former is known. θ_{1F} is the contact angle of the liquid drop on the unlimited solid surface after the completion of reaction.

5 Conclusions

(1) The nonzero resultant force of the three-phase tension at a reaction interface is the driving force for spreading and wetting of a liquid drop. On the basis of work performed by unbalanced forces, a mathematical relationship between the surface energy and the interface energy for reactive wetting is derived. The relationship is a general formulation with universal applicability, where the equilibrium Young's equation is only a special case of the energy relationship for reactive solid-liquid interfaces.

(2) The solid-liquid interfacial energy at non-equilibrium is always higher than that at equilibrium, and the difference is maximized when the contact angle is 57.36° . The solid-liquid interfacial energy at equilibrium and non-equilibrium is identical only when the contact angle is 0° or 180° , indicating that the reactive interface is thermodynamically unstable. The transition to equilibrium through interfacial reaction is inevitable and spontaneous.

(3) The reactive solid-liquid interfacial energy γ_{sl} and the solid surface energy γ_{sg} are functions of the liquid surface energy γ_{lg} and the contact angle θ . The numerical range of γ_{sl} is $0 \leq \gamma_{sl} \leq \gamma_{lg}$, and the theoretical boundary condition for the complete wetting of a liquid phase on a solid surface γ_{sg}

$= \gamma_{lg}$.

(4) The solid surface energy γ_{sg} , the solid-liquid interfacial energy at the initial state of reaction γ_{slI} , and the solid-liquid interfacial energy at the final state of reaction γ_{slF} can be solved directly by measuring the initial-state contact angle θ_1 and final-state contact angle θ_{1F} of the infinite solid-liquid wetting interface.

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