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LETTER

Dissolutive wetting of Si by molten Cu

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Dissolutive wetting occurs when a liquid spreads over a solid surface with simultaneous dissolution of the solid into the liquid. This process is of great interest for both fundamental research and several industrial processes, an important example being soldering in microelectronics fabrication processes [1]. Several studies, performed for various liquid metal/solid metal systems, have shown that for millimetre-sized droplets the spreading time in dissolutive wetting ranges from a few to several hundred seconds [2–6]. This time is orders of magnitude higher than the spreading time found in liquid metal/solid metal systems with negligible miscibility, which is typically around 10 ms [7–11]. Despite the progress made over the last 10 years in the understanding of dissolutive wetting, several points remain obscure concerning both the driving force and kinetics of this type of wetting. The aim of the work reported in this paper is to contribute to this subject by performing a comparative study of spreading on the same substrate (monocrystalline Si) at 1100 °C with pure copper and Si-presaturated copper. In the past, a similar attempt to study spreading in the same system in equilibrium and non-equilibrium conditions was made using Ag/Cu couple [12]. However, with the sessile drop technique used in these experiments, the initial stages of spreading were obscured by metal melting. In the present study this difficulty is overcome by using the dispensed drop technique, which enables the processes of melting and spreading to be separated (see for instance [13])

According to the Cu–Si phase diagram, at 1100 °C a liquid CuSi alloy containing 52 at %Si is in equilibrium with solid Si (the solubility of Cu into solid Si is negligible) [14]. As for the surface tension of pure Cu at 1100 °C, 1280 mN/m [15], it is much higher than that of molten Si, which, extrapolated to 1100 °C from the melting point of Si, is close to 800 mN/m [16, 17]. As a consequence, dissolution of Si into Cu is expected to decrease the surface tension of the liquid.

Wetting was studied in a metal furnace under a vacuum of (1–5) × 10^{-5} Pa. The experiment involved heating pure Cu or the CuSi alloy (purity higher than 99.999%) in an alumina crucible placed above the Si substrate. At the experimental temperature, the liquid was extruded from the crucible through a capillary, forming droplets with a diameter d_{dr} lying between 1.3 and 2 mm. In view of the high sensitivity of Si to oxidation and to improve surface cleaning, a prior heat treatment of the substrates was performed at 1250 °C before depositing the drop at 1100 °C.

The wetting process was filmed by a camera (500 frames per second) connected to a computer, enabling automatic image analysis. The characteristic dimensions of the drop (drop base diameter d and visible contact angle θ) were extracted with an accuracy of ±2° for θ and ±2% for d. The (111) surfaces of electronic purity Si have an average roughness of 1–4 nm after polishing with diamond paste up to 0.1 µm.

Figure 1 gives the temporal variation in contact angle θ and the normalized drop base diameter d/d_{dr} for the wetting of Si by a Cu droplet. Due to the resolution of 2 ms, most of the non-reactive spreading, which occurs at $t < 2$ ms, is missing. However, on the drop base diameter curve, it can be clearly seen that the triple line velocity vanishes at point A, corresponding to time $t \approx 4$ ms. This is just a tendency because, after slightly receding to point B, d starts to

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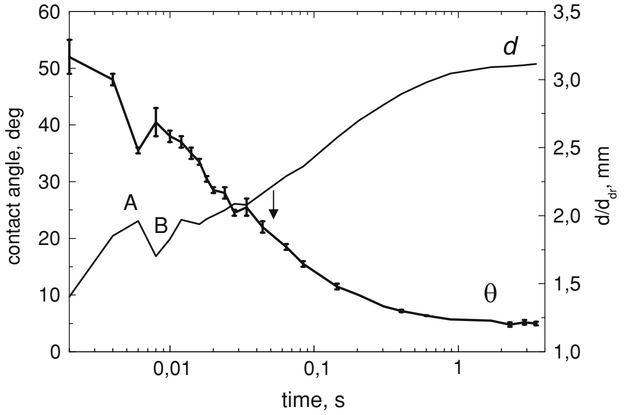

Fig. 1 Contact angle and normalized drop base diameter as a function of time plotted in a logarithmic scale for Cu on a (111) Si surface at 1100 °C. The arrow indicates the time at which the contact angle equals the value of 22° observed with Si-presaturated Cu

increase again for about 2 s before reaching a steady contact angle θ_f. The contact angle corresponding to point A, denoted θ_0, is a quasi-static advancing contact angle. Four different droplets led to θ_0 and θ_f values in the ranges 40°–50° and 5°–7°, respectively. The average value of the ratio d_f/d_{dr} (d_f being the final drop base diameter) is 3.15 ± 0.03. Figure 2 shows the SEM micrograph of the drop cross section. Due to thermal stress, several cracks appeared during cooling. In addition, the increase in alloy volume occurring during solidification is responsible for the deformation of the drop shape. Despite these difficulties one can clearly see that dissolution leads to a macroscopically non-planar interface, with a crater a few hundred microns deep formed under the drop.

Figure 3 shows the wetting curves for a CuSi alloy saturated with silicon. The values of the contact angle corresponding to point A, denoted θ_0^*, determined for four different droplets, lie between 20° and 24°. At $t < 20$ ms, both θ and d exhibit variations due to the perturbation caused by drop detachment from the capillary. This corresponds to excess energy that is responsible for the value of d at point A ($t \approx 4$ ms), which exceeds the equilibrium value d_f by 30%. The final contact angle in this system, denoted θ_f^{NR}, is very close to θ_0^*. Its value, measured for eight different droplets, lies between 20° and 24° ($\theta_f^{NR} = 22 \pm 2°$). The angle θ_f^{NR} is identified as the equilibrium (i.e. Young) contact angle in the non-reactive CuSi/Si system. The average value of ratio d_f/d_{dr} is 2.11 ± 0.10.

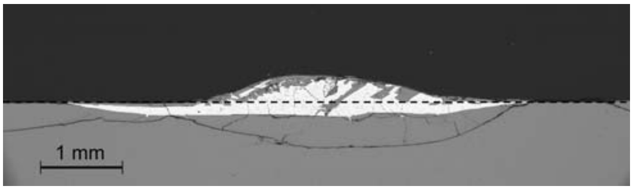

Fig. 2 Cross section of a Cu/Si sample cooled to room temperature from 1100 °C at $t > t_f$ (SEM). The dashed line indicates the initial position of the substrate surface

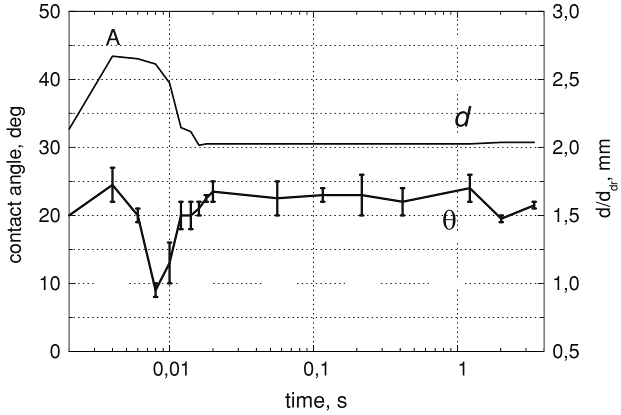

Fig. 3 Contact angle and normalized drop base diameter as a function of time plotted in a logarithmic scale for Si-presaturated Cu on a (111) Si surface at 1100 °C

The curves of Fig. 1 will be now analysed, taking into account the results of Fig. 3 for the non-reactive alloy. The quasi-static contact angle $\theta_0 = 45 \pm 5°$ is observed at a time $t_0 = 4$–8 ms that is typical of non-reactive spreading. It is assumed to be equal to or close to the contact angle of Cu on a nearly unreacted Si surface. To check this assumption, the Young contact angle $(\theta_0)_{calc}$ of pure Cu (surface tension $\sigma_{Cu} = 1280$ mN/m) in metastable equilibrium with solid Si will be calculated from the contact angle of CuSi alloy $\theta_f^{NR} = 22°$ and the surface tension of this alloy $\sigma_{CuSi} = 860$ mN/m [16, 17] by applying Young's equation: $\cos(\theta_0)_{calc} = \cos \theta_f^{NR} \times (\sigma_{CuSi}/\sigma_{Cu})$. This yields $(\theta_0)_{calc} = 51°$, which is higher than but close to the experimental value of $\theta_0 = 45 \pm 5°$.

The above considerations show that wetting in the Cu/Si system occurs in two different kinetic stages: one non-reactive and very fast, leading in a few ms to the contact angle $\theta_0 \approx 45°$; the second reactive (dissolutive), occurring in 1–2 s, leading to a visible contact angle of 5°–6° formed on a macroscopically non-planar interface. The time $t_f \approx 1$–2 s is considered to be the time needed to obtain a Si-saturated CuSi alloy by dissolution.

The reactive stage can in turn be described as occurring in two successive steps (Table 1):

Table 1 Spreading regimes in Cu/Si system at 1100 °C

Type of spreading	Spreading time (ms)	Contact angle (deg)
Non-reactive	4–8	45 ± 5
Reactive: towards interfacial equilibrium	30–50	22^a ± 2
Reactive: towards total equilibrium	1000–2000	6^a ± 2

[a] Visible contact angle

(i) The first reactive step is responsible for the decrease in contact angle from $\theta_0 \approx 45°$ (angle formed by pure copper on the unreacted Si) to 22° formed on Si by Si-saturated copper. This decrease occurs very rapidly, in only 40 ± 10 ms (Fig. 2), i.e. 25–50 less than the time $t_f \approx 1–2$ s for complete saturation of copper with silicon. Obviously, after 40 ms, solid Si is not in equilibrium with the bulk liquid. However, our results indicate that it is nearly in equilibrium with the liquid at the solid–liquid interface including the triple line region. This deduction implies that the dissolution process at the solid/liquid interface is much faster than the subsequent diffusion of Si atoms from the liquid side of the interface to the bulk liquid.

(ii) The second reactive step is responsible for the decrease in contact angle from 22° to 6° and corresponds to the formation of the crater under the drop. In view of the previous discussion, it can be concluded that spreading during this step is limited by the diffusion of Si atoms from the interface to the drop bulk. Marangoni flow can enhance the dissolution rate through fluid motion from the liquid surface close to the triple line, where the surface tension is expected to be low, to the drop top, where the surface tension is comparatively high. As for the final contact angle of 6°, due to the crater formed under the drop, this is only an apparent angle. However, one can easily verify that the decrease from 22° to 6° corresponds to a true wetting process, i.e. to increasing contact area between the solid and liquid phases. This is proved by the fact that the final value of d/d_{dr} in the reactive case exceeds the final d/d_{dr} value in the non-reactive system by 50%. As for the true final contact angle, according to Warren et al. [3] its value would be dictated by the dissolution process and not by the balance of the surface tensions at the triple junction.

It must be emphasized here that there is actually no net separation in time between the above two steps of dissolutive wetting. Indeed there is experimental evidence showing that some dissolution of Si into Cu occurs even in 40 ms, implying that the solid/liquid interface is no longer planar. However, the main cause of the changes in θ and d observed in the first, rapid step is the decrease in the surface tension of the liquid close to the triple line, while the changes in θ and d during the second, much slower step are due mainly to the formation of a macroscopically non-planar interface.

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