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Some effects of anisotropic roughening on the wetting of metal surfaces

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The wetting of aluminium, copper and steel workpieces by drops of water, tin, copper or silver–copper braze was found to be affected by anisotropic roughening.Two types of behaviour were exhibited; wetting and flow in well-wetted systems with contact angles below about 20° was enhanced by the roughening, but that of poorly or moderately wetting systems was impeded. The anisotropy of the roughening was reflected in the eccentricity of the drops which increased with roughening, particularly so for well-wetting systems. Similarly, the area covered by a drop was little affected by roughening for most systems, but increased rapidly for those that wetted well. These experimental effects were in accord with models that regard roughening surfaces as presenting a series of energy barriers impeding the flow of all but the most energetic liquids, as defined by their enthalpy.

1. Introduction

The effectiveness of brazing and soldering processes depends critically upon the ability of joining metals or alloys to wet the workpiece surfaces. However, the achievement of good wetting is not always easy and care must be devoted to the preparation of workpiece surfaces since their cleanliness and roughness can affect liquid flow behaviour. While there is a wealth of technological experience, relatively few quantitative studies of the effects of roughening on the wetting behaviour of solders and brazes [1–3] have been reported and attempts to discuss roughening effects in scientific terms [4] have had to draw largely upon models and theories developed from observations made on non-metallic systems.

Early modelling of surface roughness phenomena led to starkly differing predictions of the behaviour of wetting liquids; Wenzel's treatment, which regarded the increase of surface area as the prime effect of roughening, suggested that wetting would be enhanced [5] while other analyses, paying particular attention to individual asperity geometry, led to expectations of a decrease [1, 6]. However, this discrepancy has been resolved by recent theoretical studies comparing an array of surface asperities to a series of energy barriers that an advancing liquid must overcome [7–9]. The more energetic a liquid is, as measured by its enthalpy, the less significant is the geometric impedance to flow of an individual asperity and the closer the predicted behaviour resembles that of the Wenzel model [5]. Whether such energetic concepts are relevant to the wetting and spreading of metal melts on metallic substrates is not certain, although a few data gathered during a previous study of the wettability of ceramics suggests that this could be so [10]. The objective of the work described in this paper was an exploration of this possible relevance, and hence more data were sought, specifically for anisotropically roughened surfaces typifying those of workpieces used with brazes and solders.

2. Experimental materials and techniques

Substrates with varying degrees of anisotropic surface roughness were used. For convenience, the axes of the valleys will be referred to as the *B* direction and their normals as the *A* direction.

Commercial purity copper was abraded with alumina grits, aluminium was lathed using differing cuts and traversing speeds, and mild steel and stainless steel (AISI 321) were ground with diamond wheeels. These roughened surfaces were characterized using a Surfcom 30B stylus profilometer; the average parameters summarized in Tables I and II were derived from the results of at least three traverses, with a usual precision of better than ± 10%. After this surveying, the workpieces were cleaned by ultrasonic agitation in acetone and dried with a hot air blast before being used in the wetting tests. These measured wettability in terms of the contact angle, θ, assumed by a drop resting on a horizontal substrate (Fig. 1), wetting being signified by an angle of less than 90° and improving as this approaches 0°. The drops, centrally located on all but the aluminium workpieces, were of analytically pure water or spectroscopically pure copper or tin. The contact angles quoted later normally are the averages of three to five separate experiments and have a precision of better than ± 1.5°.

Tests with water were conducted at room temperature in an open laboratory, drops nominally 0.035 ml being dispensed on to the substrates from calibrated pipettes. The drops were viewed and photographed in both the *A* and *B* directions using a 35 mm camera. With tin, a more elaborate procedure had to be adopted using the device sketched in Fig. 2. After 0.035 ml tin had been loaded into the device with the rod down and blocking the bottom hole, the dispenser was fitted to the top plate of a vacuum furnace equipped with diametrically opposed observation ports. The furnace chamber was evacuated to less than 10^{-5} mbar and

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TABLE I Wetting data for water and tin drops dispensed on to copper and aluminium workpieces

Roughness parameters measured normal to the abrasion or grinding direction			Wetting parameters: water				Wetting parameters: tin				
			Contact angle (deg)		Spread		Contact angle (deg)			Spread	
R_a (μm)	λ_a (μm)	α (deg)	θ_A	θ_B	Area (mm^2)	Eccentricity	θ_A 1 min	θ_A 45 min	θ_B* (45 min)	Area (mm^2)	Eccentricity
Abraded copper											
0.62	53.4	5.5	42.5	38.5	46.3	1.16	51.5	30.5	39.0	52.3	1.05
1.46	59.0	8.4	46.0	43.0	44.1	1.08	53.0	41.0	38.0	45.1	1.06
1.58	61.0	9.4	44.5	42.0	48.5	1.22	52.5	40.5	38.5	47.8	1.04
2.08	70.4	10.1	45.0	42.5	45.7	1.15	52.5	41.0	38.0	45.0	1.04
2.19	77.8	10.1	44.5	43.0	45.1	1.17	53.0	42.0	38.0	45.5	1.05
2.60	93.0	10.1	48.0	41.0	41.4	1.25	54.0	41.5	38.5	43.8	1.09
4.94	121.4	14.9	53.0	41.0	47.0	1.29	56.5	43.0	34.0	46.1	1.08
Machined aluminium											
0.42	39.5	3.5	10.0	9.5	80.1	1.04	40.5		38.2	57.0	1.04
2.02	49.5	13.9	12.5	9.5	74.1	1.30	45.0		43.0	55.5	1.07
2.21	41.5	20.2	11.5	8.0	81.8	1.48	50.0		43.5	61.7	1.09
10.1	106.0	34.4	13.5	8.0	76.8	1.65	55.0		44.0	48.5	1.22
32.3	291.0	40.1	13.5	6.5	81.4	2.06	62.0		37.7	50.4	1.49

*Estimated from eccentricty data

power supplied to its heating elements to melt the tin and raise the workpiece temperature to 250° C while outgassing took place. The temperature was then increased rapidly to 500° C, the rod lifted using a magnet and molten tin dispersed on to the workpiece. The observation ports were used to back illuminate and photograph the *A* direction drop profile. Subsequently, the *B* and *A* direction diameters of solidified tin drops were measured and their peripheries examined using scanning electron microscopy. A few samples were cross-sectioned, polished and examined optically for evidence of chemical interaction between the tin and the substrates.

The higher melting point of copper, 1083° C, made the dispensing device awkward to use, and conventional sessile drop tests were employed. A small, 0.0034 g, disc of copper was centred on the 15 mm × 15 mm workpiece substrate, the furnace chamber was evacuated to 1 to 2 × 10^{-5} mbar and power was supplied to heat the sample to the experimental temperature, with pauses for outgassing at 250 and 500° C. The sessile drops were viewed and phtographed in the *B* direction during the 15 min hold at 1100° C, but the contact angles were too small to be measured accurately, and the data quoted later were calculated from the dimensions of the solidified drops.

TABLE II Wetting data for sessile drops of copper on stainless steel and mild steel workpieces

Roughness parameters normal to the abrasion or grinding direction			Wetting parameters: copper drops				
			Contact angle (deg)		Spread		$R_{\cos}\theta_0$ (deg)
r_a (μm)	λ_a (μm)	α (deg)	θ_A	θ_B	Area (mm^2)	Eccentricity	
Stainless steel							
0.24	52.1	1.7	7.5	7.3	5.0	1.03	0.9998
0.91	108.5	3.1	6.9	6.7	5.3	1.04	1.0082
1.26	102.7	4.6	1.6	0.7	18.2	1.80	1.0168
1.99	82.4	8.8	0.3	0.1	54.1	2.21	1.0234
Mild steel							
0.25	67.4	1.3	1.1	0.6	18.7	1.03	1.0080
0.61	105.0	2.1	0.5	0.3	37.5	1.89	1.0127
0.75	55.2	4.9	0.2	< 0.1	98.2	23.90	1.0302

3. Results

3.1. Surface roughness measurements

All three preparation techniques produced marked anisotropy of surface texture, the valleys following the direction of the machining tool or the abrasive strokes. The *A* direction amplitude (R_a), wavelength (λ_a) and steepness (α) parameters all varied similarly, (Tables I and II), but following the practice developed in an earlier study of the wetting of ceramic surfaces [10], the principal texture parameter with which variations in wettability were compared was the steepness, α. The results of stylus profilometry in the *B* direction were variable but indicated that the surface preparation techniques had not caused significant bumpiness, the slopes of such features as were revealed averaging no more than 1°.

3.2. Dispensed drop tests

Water drops assumed stable profiles within 1 or 2 sec of being dispensed on to copper or aluminium workpieces. The wetting of copper was good and even that of the roughest aluminium workpiece with an α of 40.1° was excellent (Table I). The drops spread further in the *B* than *A* direction, and Fig. 3 shows that this eccentricity varied similarly for both workpieces. The *A* direction contact angles of drops on copper workpieces were increased progressively by roughening, but those of drops on aluminium workpieces were little affected (Fig. 4). There was also a slight increase in the *B* direction angles for copper and a decrease for aluminium workpieces.

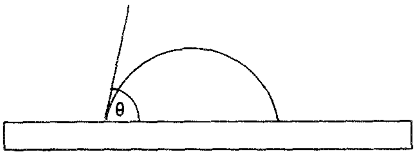

Figure 1 Schematic profile of a sessile drop.

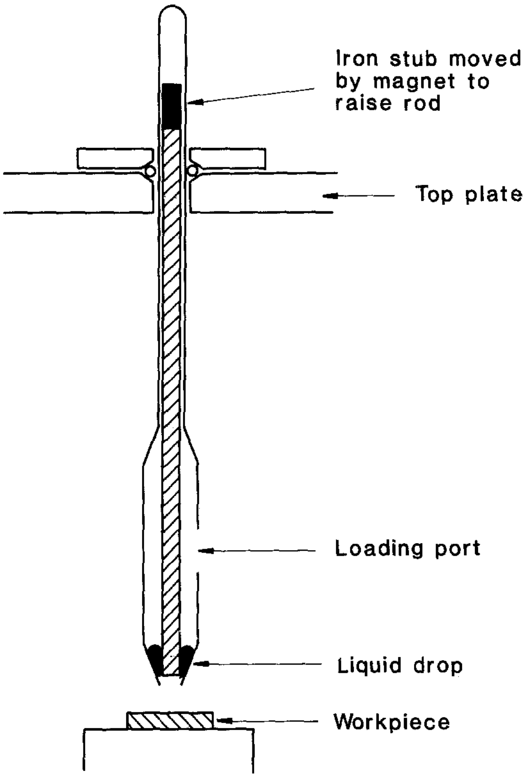

Figure 2 Schematic arrangement of the molten tin dispenser.

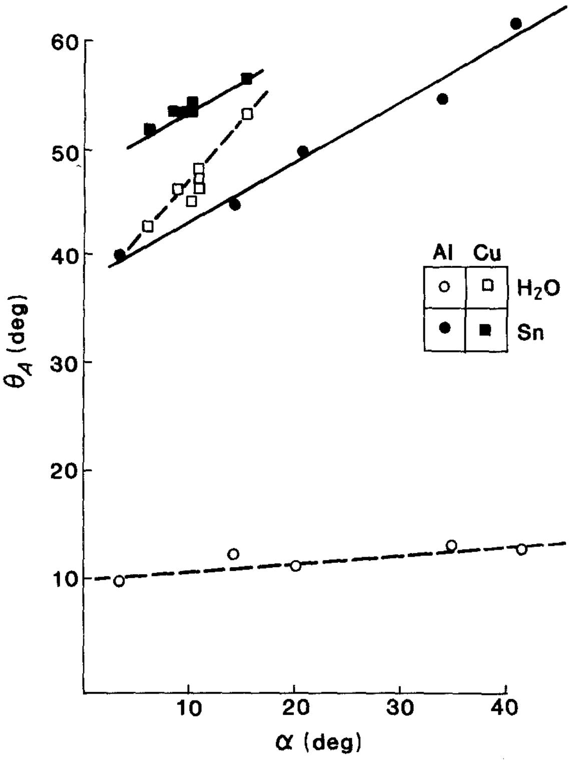

Figure 4 The effect of asperity steepness on the wetting of copper and aluminium by drops of water or tin.

Tin drops assumed stable profiles within a minute, although these were not always symmetrical for aluminium workpieces. No significant changes were observed during the remaining 44 min of the hold time for drops resting on aluminium substrates, but the peripheries of drops on copper crept forward progressively. Tin wetted both substrates, spreading more readily in the *B* than the *A* direction (Table I). The eccentricity of the drops increased with substrate roughening (Fig. 3), but there was no significant change in the total area covered by the drops.

The average *A* direction contact angles on aluminium increased linearly from 40 to 62° as the valley sides steepened to 39° (Fig. 4). However, the wetting of copper substrates was influenced by both the surface roughness and contact time. The *A* direction contact angles progressively increased but the estimated 45 min *B* direction angles were decreased with substrate roughening, Table I. The *A* direction contact angles were measured after 45 rather than 1 min were smaller by about 10° and displayed diminished sensitivity to substrate roughness.

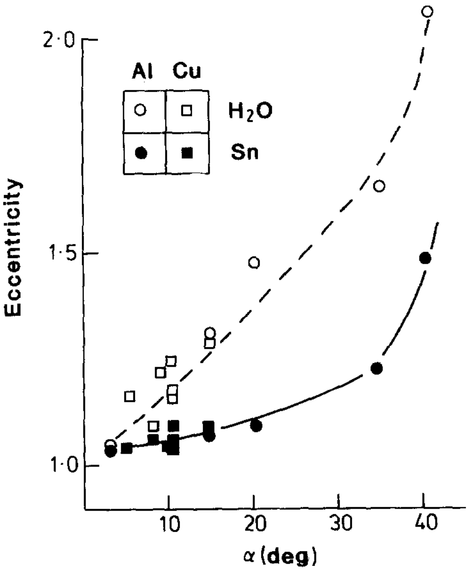

Figure 3 The influence of *A* direction asperity steepness on the eccentricity of water and tin drops dispensed on to aluminium and copper.

SEM studies of solidified tin drops confirmed the preference for the liquid to flow along valleys (Fig. 5), particularly on the rougher aluminium workpiece. There was some crazing of the alumium surface ahead of the drop and optical studies revealed evidence of erosion. Similar studies of tin on copper revealed evidence of chemical interaction at the drop peripheries and the occasional tongue of reaction product could be seen extending along an abrasion valley. Optical microscopy of cross-sectioned samples showed that there had been considerable erosion of the copper and formation of reaction product needles and layers (Fig. 6).

3.3. Sessile drop tests

While not checked rigorously, the copper sessile drops assumed stable profiles within about 2 min of achieving their experimental temperature. The wetting of both workpiece materials was excellent, with many of the contact angles being less than 1° (Table II). This near perfect wetting was associated with marked eccentricity of the drops when the average asperity slope exceeded 2 or 3° (Fig. 7), and, unlike the dispensed tin drops, there was a progressive and rapid increase in surface coverage with roughening (Fig. 8). The contact angles assumed by the liquid fronts advancing in both *A* and *B* directions were decreased by more severe

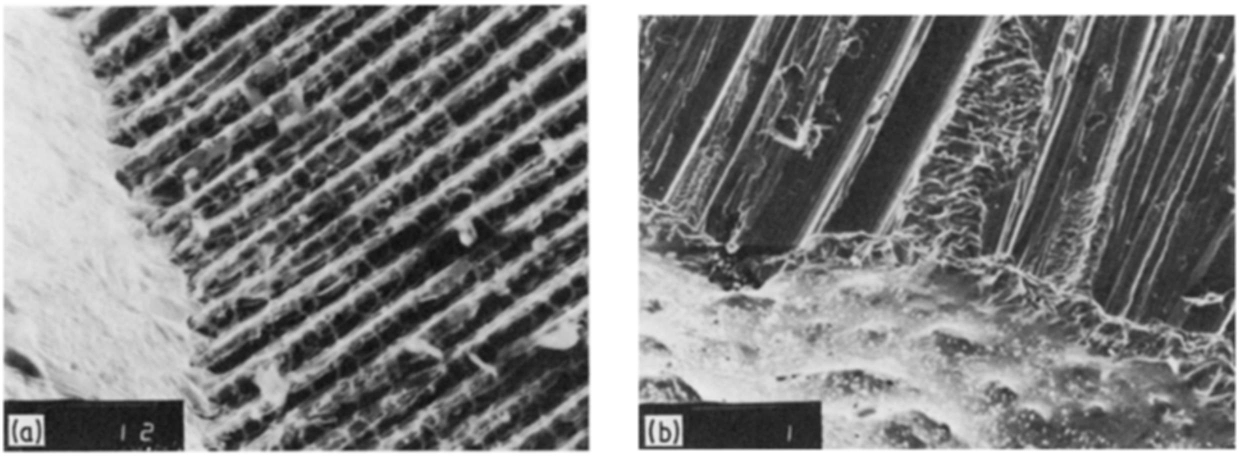

Figure 5 Scanning electron micrographs of the periphery of a tin drop on (a) aluminium with an α of 13.9° and (b) copper with an α of 14.9°. × 140.

roughening, as shown in Fig. 9 for copper, but the values for the *A* direction were always slightly larger.

4. Discussion

The data presented in this paper demonstrate that roughening metal surfaces can affect their wettability and provide evidence quantifying some effects of anisotropy. In attempting to understand these results, it is necessary to consider both the general effects of surface roughness revealed by the data as well as the particular effects associated with specific systems.

The *A* direction contact angle data summarized in Table I, and those presented in Table III which have been described in a previous paper [10], are gathered together in Fig. 10. These plots demonstrate that with non-wetting, or moderately wetting systems there is a simple linear relationship between the observed contact angles and the steepness of the asperities on the workpiece substrates. The slopes of these relationships vary from system to system, but those for tin on copper and aluminium are similar, as are those for water on copper and nickel. In contrast, if the liquid wets with contact angle of less than about 10° on a smooth surface, roughening enhances this behaviour.

Both types of behaviour can be compared with the predictions of theoretical models [7–9] that treat asperities as energy barriers impeding flow to an extent dependent on the energy of the liquid. Considering first the experimental behaviour of non-wetting and moderately wetting systems, it can be seen from Fig. 10 that their *A* direction contact angles were linear functions of the steepness of the surface roughened asperites. The slopes of the data for tin on aluminium and copper after 1 min, two relatively unreacted systems, are in good accord, as are those for water on nickel and copper but not aluminium, for reasons to be discussed later. Thus, there is evidence that the effect of surface roughness on wetting behaviour is a function of the chemical nature of the liquid rather than of the solid substrate. The energy of a liquid can be measured in terms of its enthalpy [10], calculated from specific heat and latent heat data, and comparison of the variation in wettability with surface roughness. The slopes of the Fig. 10 plots, with the enthalpies of the liquids, yields a simple relationship. As shown in Fig. 11, this is of the form

$$\frac{d\theta_A}{d\alpha} = \frac{S_H}{E_H}$$

where E_H is the enthalpy and S_H a constant equal to 10.6 kJ mol^{-1}. This relationship is virtually identical to that observed for isotropically roughened ceramic substrates, indicated by the dotted line in Fig. 11. However, in contrast, the effect of roughening on *B* direction behaviour was, ultimately, to enhance flow and hence minimize the potential energy increase caused by *A* direction restrictions. This differing behaviour of advancing fronts caused the drop contact areas to be eccentric to an extent dependent on

TABLE III The influence of anisotropic roughening of nickel workpieces on their wetting by copper and mercury

α (deg)	Copper contact angle (deg)		Mercury contact angle (deg)
	θ_A	θ_B	θ_A
0.3	19	19.5	–
1.6	18.2	17.5	139
3.3	18.5	16.1	143.8
5.7	20.1	16.6	137.2
10.1	21.5	13.5	154.5

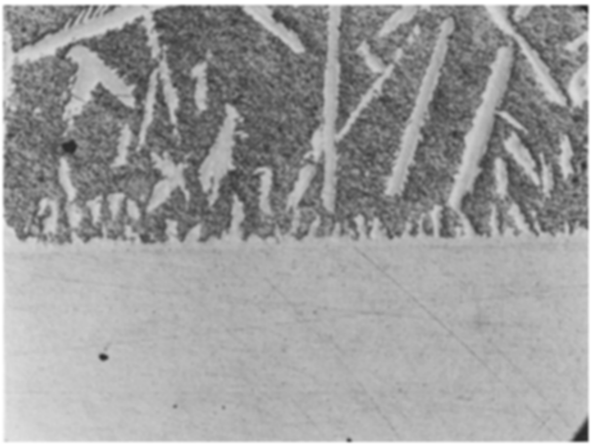

Figure 6 Cross-section through the interface formed by a tin drop and copper workpiece with an α of 5.5°. × 31.

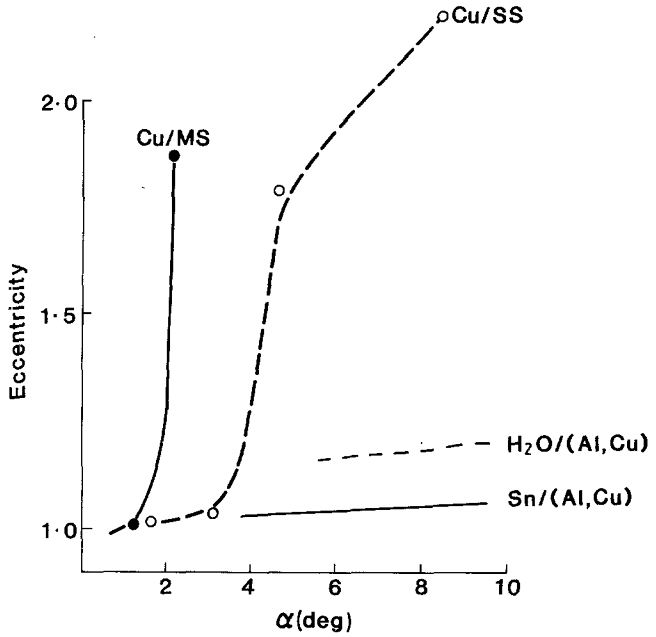

Figure 7 The influence of workpiece roughness on the eccentricity of copper sessile drops resting on mild steel and stainless steel. Data from Fig. 3 for water and tin drops on aluminium and copper workpieces included for comparison.

both the chemical nature of the liquid and the temperature (Fig. 3). There are, therefore, similarities between contact angle and eccentricity data. Whether the specific influences of factors such as liquid enthalpy on eccentricity are similar is a matter for investigation.

Turning now to the behaviour of very well-wetting liquids, it is noteworthy that roughening enhanced their flow in both *A* and *B* directions. The energetic barrier treatment of rough surfaces predicts that wicking, unimpeded flow, will occur if an increase in the spread always decreases the total energy of the system, if the energy decrease produced by changing a free solid surface into a wetted interface is never balanced by an equal increase in the energy of the extended liquid surface. Thus roughening can promote wetting since it increases solid surface and interfacial areas relative to that of the smooth covering liquid. Quantitatively, the treatments predict that spontaneous wicking will occur if

$$R \cos \theta_0 > 1$$

where R is the relative area of the solid surface and θ_0 the contact angle on a completely smooth surface. In practice, our well-wetted substrates exhibited wicking when α was greater than 3.1° for stainless steel or 1.3° for mild steel (Table II). These experimental observations can be compared with calculated $R \cos \theta_0$ data using extrapolations of the wetting data plotted in Fig. 9 to obtain θ_0 values and approximating the *A* direction surface topography to a sine wave to derive R values. The results of these calculations are listed in Table II and comparison with the experimental observations of wicking suggests a threshold $R \cos \theta_0$ of 1.01 rather than the theoretical 1.00. Such calculations also predict that water should have wicked on the aluminium workpieces, but as shown in Table I and Fig. 10, the contact angles neither increased as they had done with copper and nickel workpieces nor decreased dramatically as with the wicking systems. Why water–aluminium displays such indeterminate behaviour is not clear, and the problem was not studied in detail because the system was outside the main material interests motivating this work. With these

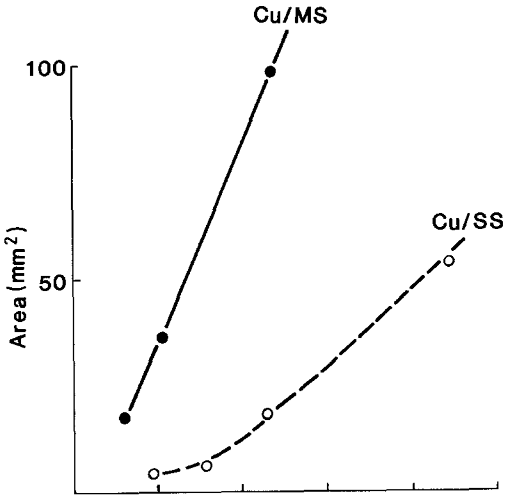

Figure 8 The influence of workpiece roughness on the spread of sessile drops of copper resting on mild steel or stainless steel.

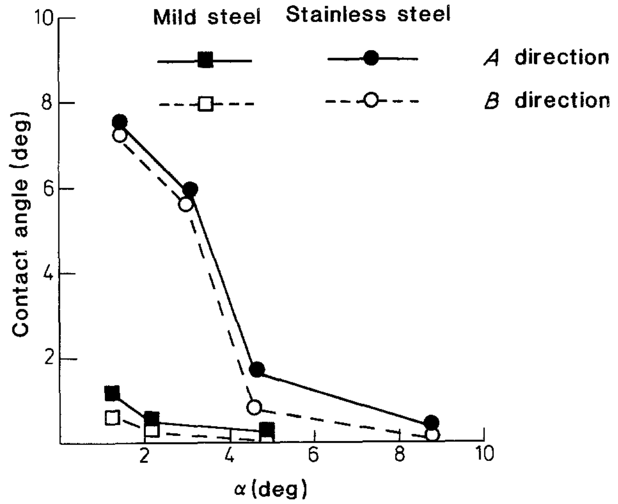

Figure 9 The effect of workpiece roughness on the wetting of stainless steel and mild steel by sessile drops of copper.

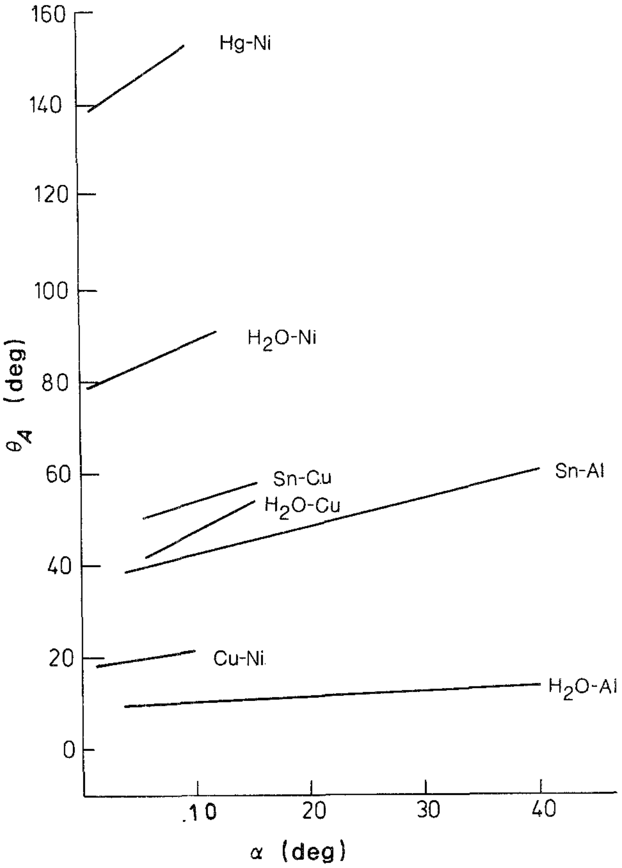

Figure 10 Summary of the effects of workpiece roughness on wetting by water and several molten metals.

qualifications, the behaviour of the well wetting systems is also in accord with the energetic mode which predicts that roughening should enhance flow. The actual contact angles resulting from this flow, however, are difficult to predict since they depend on kinetic factors such as viscosity, evaporation and, probably, most importantly in these experiments, melt–workpiece interdiffusion which can consume the liquid and/or raise its melting point. The severity of this effect as a flow limitation depends on the specific characteristics of a system, and having discussed some general matters, it is worthwhile considering such characteristics.

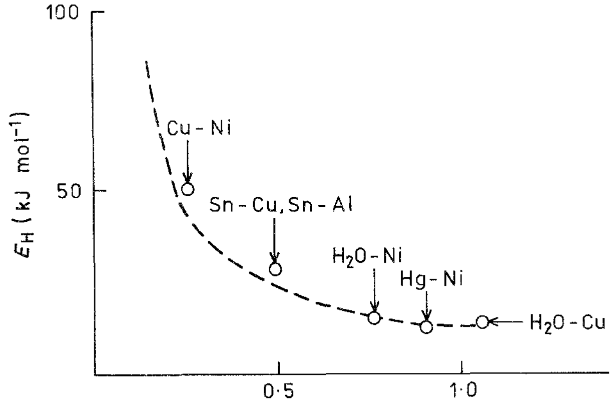

Figure 11 Correlation of the enthalpies of liquids with the extent to which their *A* direction wetting behaviour is influenced by anisotropic roughening of metal workpieces. The dotted line refers to earlier work with isotropically roughened ceramic workpieces.

The simplest experiments conducted in this programme used water as the liquid, and it is noteworthy that the differing wettabilities of aluminium and copper demonstrate the influence of surface oxide films. It is generally accepted that metal oxides are wetted by water, a polar liquid, and the poorer wetting of copper may reflect its lesser ionicity, predictions of 55% for Cu–O as opposed to 63% for Al–O being derived from Pauling's suggested relationship with electronegativity differences. (It is interesting also that the Pauling [11, 8] treatment predicts the observed poorer wettability of nickel [12].)

Of more technical relevance is the behaviour of the liquid metals, and it is noteworthy that while their behaviour could be generally accounted for by existing theoretical models, these assume that the liquid–solid systems are inert and this is not true for most of those discussed in this paper. Thus aluminium and copper are soluble in tin up to concentrations of about 25 at % at 500° C [13] and these workpieces were eroded during the wetting tests. Furthermore, tin forms intermetallics, Cu_4Sn and Cu_3Sn, with copper at 500° C and their formation at the drop peripheries led to a secondary spreading that greatly modified workpiece roughness effects on wetting after contact times of 45 min. No intermetallics are formed in the tin–aluminium system, but the liquid tunnelled under the suface oxide on the workpieces to create a crazed network as discussed elsewhere [14]. Similarly there is some mutual solubility in the copper–iron system, about 7 at % in both the liquid and solid at 1150° C [13], but in practice this did not restrict the flow of copper on mild steel or stainless steel workpieces either by absorption of the liquid or increasing its melting point. As might be expected, the good wetting of the steels by copper was accompanied by some grain-boundary penetration, a common observation for brazed joints and an effect of importance during the reheating of copper steels. Reference has been made also to the completely soluble, poorer wetting, copper–nickel system for which there is quantitative evidence [15] that interdiffusion causes secondary spreading, but only to the extent of about 0.1 mm in the conditions used in the present work. All these effects, therefore, while of some interest and potential importance, were minor compared to those attributable to workpiece roughening.

The implications of this work for soldering and brazing have yet to be studied in detail, but it is clear that anisotropic workpiece roughness can have a major influence on the nature and extent of liquid flow in broad accord with models and theories developed initially for chemically inert liquids in contact with isotropically roughened non-metallic substrates. The factors influencing flow behaviour, apparently, are not very system specific. However, whether roughening assists or impedes flow depends critically on the inherent wettability of the system, the data suggesting that enhanced flow will result if θ_0 is below a value of about 10°. Thus different surface preparation procedures may be beneficial when using very well-wetting solders and brazes, typified by the main commercial materials, and those with marginal wettability, such as experimental alloys intended for joining exotic workpieces or new formulations dispensing with hazardous, scarce or expensive components.

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