Electronics Materials - Microstructure of surfaces

Grain boundaries

In Metals basics we will be describing how metals solidify, in a process which involves nucleation and the growth of crystals or grains. When we etch the solder surface, we observe a network of grains separated by grain boundaries. The initial solid nuclei (there will be millions of them!) can often start as tree-like shapes that we call dendrites (Figure 1).
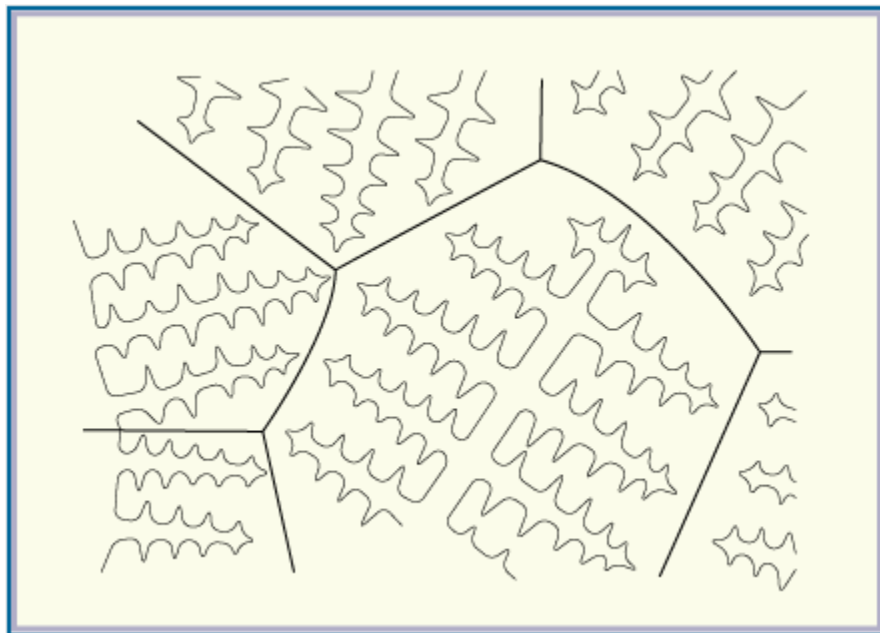

Figure 1: Dendrites and grains

Once nucleated, the dendrites spread sideways and the secondary arms generate further tertiary arms and so on. When solidification is complete, all the dendrites that have formed knit together to form grains (or crystals). By cooling more quickly, a smaller grain size results and this has the effect of making the resulting solid stronger. Figure 2 and Figure 3 are examples of metals with different grain size – the one exhibited in Figure 3 will be significantly stronger than its counterpart in Figure 2.
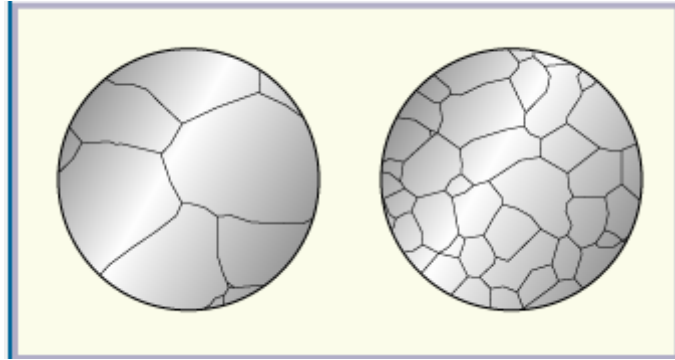
Figure 2: Large grain size, Figure 3: Small grain size

The strength of the metallic material can be linked to the grain size via the Hall-Petch equation:

$$\sigma_y = \sigma_o + k/\sqrt{d}$$

where sy is the yield strength, so and k are material constants and d is the average grain diameter.

The role of grain boundaries is an important one in many phenomena – such as diffusion, corrosion and creep. Grain boundaries are regions of local atomic disorder and are convenient paths for accelerated diffusion to take place. In addition, these boundary locations are regions of high energy and react preferentially when subjected to acid attack (etching). High temperature service conditions[1] can result in creep strains and these strains take place via grain boundary sliding.

[1] As explained in Mechanical properties of metals, all solders are operating at temperatures which are high when compared with their melting points.

 In order to examine the grains and grain boundary appearance of metallic surfaces, it is first necessary to grind and polish the surface to a mirror-like finish. Then, the surface must be etched. The choice of etchant will depend on the nature of the material but the principle of all etchants is the same – there will be a preferential attack at crystal grain boundaries. Often, the attack produces a faceted surface and the orientation of these facets will vary from grain to grain. As a result, the amount of reflected light reflected into the objective lens of a microscope will vary between grains and grain boundaries (Figure 4).
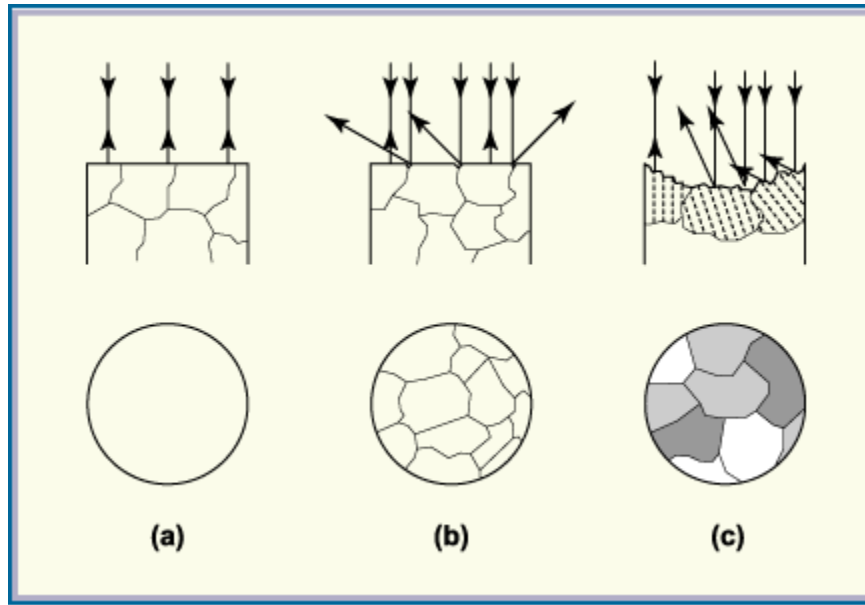
Figure 4: Polished and etched surfaces

Figure 4(a) exhibits a polished metal surface (unetched) with no microstructural detail revealed, Figure 4(b) shows an etched surface and reveals grain boundaries, while Figure 4(c) reveals grain shading and grain boundaries as a result of further etching. In this last example, the amount of reflected light captured by the objective lens of the microscope will vary from one grain to another. This will lead to some grains appearing to be light in colour and others appearing dark – even though all the grains may be identical in composition and type.
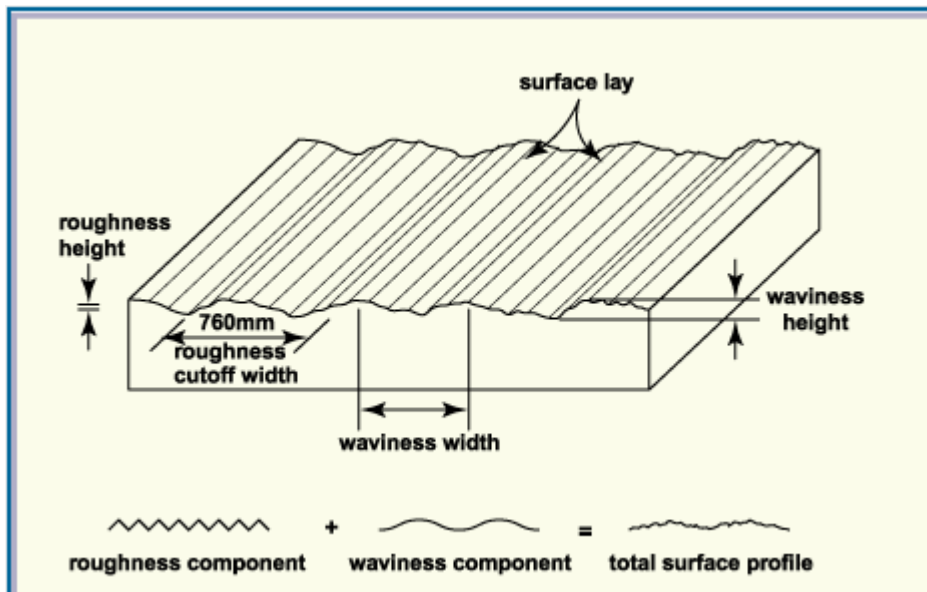
Surface texture

Figure 5: Components of surface topography

The surface characteristics of materials are often important and the most commonly specified parameters are roughness, waviness and lay (Figure 5). Perhaps the most important of these is roughness and this is usually expressed as the arithmetic average (Ra) of the peak-to-valley height of surface asperities in microns (μm). Traditionally, the surface roughness has been measured using a profilometer that electronically measures surface texture using a stylus – not unlike that used in record-players. Since a profilometer stylus has a finite radius (around 2.5 μm), it cannot reach the bottom of valleys of surface features, and so cannot measure true depth. The Ra roughness is only approximately 25% of the true peak-to-valley height.

Atomic force microscopes, which came into widespread use in about 1990, are available with surface styli having radii as small as 10 nm ($1×10–8$ m) and as such produce truer representations of surface features [2].

[2] One unit of measurement you will come across when dealing with very small dimensions, especially for wavelengths of light or interatomic distances, is the Angstrom Unit (symbol Å), named after the 19th-century Swedish physicist Anders Jonas Ångström. 10 Å = 1 nm. Angstrom Units are often a convenient measure, because atoms are typically 1 Å across.

Scanning electron microscopy (SEM) is used like optical microscopy to show the topological features of surfaces. It can be used for magnifications that are outside the realm of optical microscopy (greater than ×3,000) and it also gives a depth of field that shows features that cannot be resolved by conventional optical techniques. Many SEM units are now also equipped with an Energy Dispersive X-Ray Analysis[3] (EDXA) facility – also known as EDAX – that will produce quantitative information on the chemical composition of surfaces.

[3] Visit http://www2.rgu.ac.uk/life_SEMWEB/xray.html for an explanation of how this technique works.

Bonding to surfaces

It is very important that any solder joint bonds well to the two or more surfaces that it is joining. The main adhesion mechanisms that can be involved in such bonds are:

- Mechanical interlocking – this is a kind of 'velcro' effect, where the liquid penetrates the surface layer of the surface and then solidifies to form an anchor on the substrate.

- Inter-diffusion – this exchange of atoms between the surfaces is prominent at higher temperatures and mainly involves liquid/solid interactions.

- Chemical interaction –which results in the formation of a strong, but often brittle, inter-metallic compound, as will be described later in Solder joints.

The last of these is the main mechanism in solder joints, and is related to the way in which the solder 'wets' the surface. There is some more about this in the section on Surface energy and wetting, and plenty more to come!

The first two of these mechanisms are also affected by the nature of the surface. For example, mechanical interlocking is enhanced by surface roughening, which is why surfaces being prepared for adhesive attachment are usually roughened either mechanically or chemically, or by a combination of both.

Diffusion processes

To see what kind of surface might best promote inter-diffusion, we need to learn a bit more about diffusion processes. These processes will also be involved in our later consideration of reliability and failure.

In the case of a solder joint, inter-diffusion will be dominated by vacancy or substitutional diffusion. This mechanism occurs between atoms of similar size and crucially relies on the presence of vacant lattice sites ('vacancies') in the crystal structure. As the temperature rises, atoms gain vibrational energy and there is a much greater chance of them being 'vibrated away' from their lattice site, thereby creating a new vacancy. For this reason, the number of vacancies increases exponentially with temperature. The diffusion across a solder-substrate interface will involve such mass transfer, particularly from the liquid solder into the solid substrate.

There are two types of diffusion systems – steady state and non-steady state - and the kinetics of these systems are defined by Fick's Laws. Fick's First Law is that the flux or flow of atoms in steady state diffusion can be represented by the equation:

$$J = -D\frac{dC}{dx}$$

Where

J = the flux or net flow of atoms

D = the diffusion coefficient of the system

C = the concentration of the diffusing species

(dC/dx is the concentration gradient)

Steady states are not commonly encountered in 'real' situations, so Fick's Second Law of diffusion4 – for non-steady state conditions – is often more appropriate for engineering:

$$\frac{dC}{dt} = \frac{d}{dx}\left[D\frac{dC}{dx}\right]$$

This equation indicates that the rate of compositional change is determined by both the diffusivity and the rate of change of the concentration gradient. In soldering, we would expect there to be differences in diffusion depending on the solder type, and whether fresh solder is in contact with the surface (as with wave soldering) or not (as with reflow soldering). Intimacy of contact is a key for effective diffusion, so the surface needs to be smooth, rather than rough.

4 The derivation and solving of this differential equation is outside the scope of this note.

Surface energy and wetting

The wetting of the surface by solder is an essential ingredient in making possible chemical interaction such as the formation of intermetallics. In Effects at liquid surfaces you will already have studied the concept of the wetting of surfaces: essentially, for a liquid (such as molten solder) to wet a solid surface (such as a copper substrate) there has to be an overall decrease in surface energy. This is shown in the following equation:

where gLV, gSL and gSV represent the surface energies at the liquid/vapour, solid/liquid and solid/vapour interfaces respectively.

To promote wetting, we can:

- make gLV low by choosing a liquid with low surface energy or by having a high local concentration of vapour
- make gSL low by choosing a liquid which is chemically similar to the solid
- make gSV high by choosing a high surface energy solid which is chemically dissimilar from the vapour.

These guidelines show why, for example, molten polyethylene will wet solid alumina, whereas molten iron will not (see the surface energy values in Table 1).

Table 1: Some surface energy data[5]

material	surface energy, g_{SV} at 300K (mJ/m^2)	surface energy, g_{LV} at 1.1T$_m$ (mJ/m^2)
polyethylene	33.5	26.5
printed circuit board	46.2	46
alumina	638	700
iron	2300	1835
tin-lead solder		

[5] Note that metals and ceramics generally have high surface energies whilst those of polymers are generally low.

However, other factors such as pressure and substrate texture also have an influence on wettability. In Effects at liquid surfaces, we used an alternative way of looking at wetting, from the perspective of surface free energy. Figure 6 shows a droplet of liquid moving outwards, and increasing the area of its top surface (AL) by an amount DAL. As a result of the spread, the surface area of the substrate (AS) is reduced by DAS, which of course is the same as the increase in the contact area between droplet and substrate.
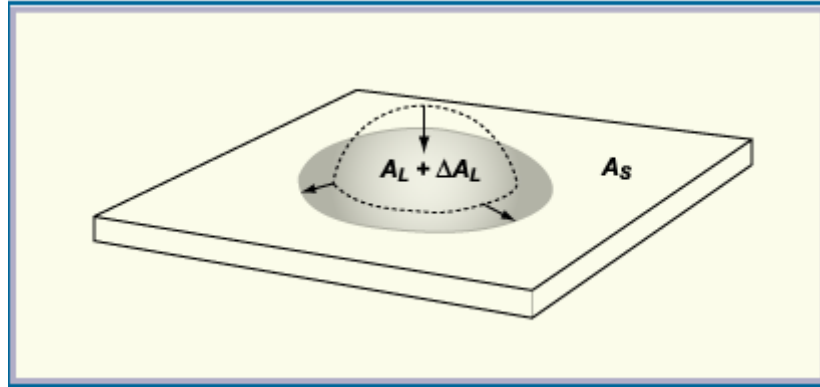
Figure 6: Spreading of a droplet

We derived an equation for the change in surface free energy DE:

$$\Delta E = \gamma_{LV}\Delta A_L + \gamma_{SL}\Delta A_S - \gamma_{SV}\Delta A_S \qquad \text{(Equation 1)}$$

For wetting to take place, this surface free energy must be negative, that is

$$\gamma_{LV}\left[\frac{\Delta A_L}{\Delta A_S}\right] < \gamma_{SV} - \gamma_{SL} \qquad \text{(Equation 2)}$$

For a rough surface, the area to be wetted (DAS) will be larger than the area of liquid required to cover it (DAL) – as shown in Figure 7.

Figure 7: A larger solid surface area (energy) being covered by a lower surface area (energy)
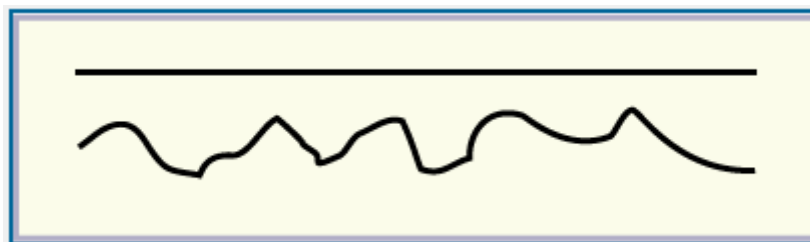
Figure 7: A larger solid surface area (energy) being covered

For rough surfaces, DAL/DAS will be less than 1, so that the left hand side of Equation 2 will reduce in value. Thus, for unchanged values of surface energy, the driving force for wetting will be increased.

Surfaces and plating

You will already know that there are two important ways of electrodepositing metallic surfaces onto printed circuit boards (electroless deposition and electroplating), and it is important to carry out the correct procedures for preparing the substrate surfaces for accepting the metallic deposition. In the case of electroless plating deposits, adhesion is by mechanical bonding, and the acid etch stage in the process is important because it roughens the substrate surface and provides more bonding sites.

A wide range of metals and alloys can be electrodeposited, but the bond strength will depend on the chemical nature of the substrate. A good electroplated layer will have a bond strength in shear of more than 140 MPa. The adhesion mechanism for electroplating is part mechanical and part chemical bonding. However, to make the latter possible, the substrate must be atomically clean: there can be no adsorbed oxide layers or films of any sort!

This is where the 'plateability' of metals becomes a factor. Very corrosion-resistant metals such as titanium, stainless steels, tantalum and aluminium often have passive surfaces composed of oxide films. It is difficult to remove these, and thus these metals are difficult to plate.

Note that the physical nature of a surface (roughness, waviness etc.) determines largely what the electrodeposited surface will look like. For example, if a shiny chromium plating is necessary, the metal must be polished before the plating operation.

Wear

Wear is the removal of material from a surface as a result of its movement relative to other surfaces. Whilst more obvious in rotating machinery, wear is a factor determining life expectancy in electronic applications such as connectors, relays, switches and variable resistors.

Four main wear mechanisms occur in electronics:

- **Adhesive wear** occurs when smooth surfaces rub against each other. The contact load causes high spots on the surfaces to make contact with each

other, and relative motion causes local heating and dragging between the surfaces. In some cases, particles will be broken off, resulting in debris; in others, a 'cold weld' may occur, binding the surfaces together

- **Fretting** is similar to adhesive wear, but occurs when surfaces are subjected to small oscillatory movements which prevent the debris escaping from the wear region, so that particles are broken up further and may become oxidised. The repeated movements may also result in some surface fatigue

- Abrasive wear occurs when the relatively soft surface is scored by a relatively hard surface, and is basically a cutting action, often accompanied by the displacement of the soft material at the sides of grooves scored in it

- Corrosive wear involves electrolytic action removing material from the surface. It becomes especially important when other wear processes have removed protective films, leaving the surface in a chemically active condition. Corrosion can then be a powerful additive to other wear mechanisms.

This last is just one example of a case where more than one mechanism operates in a situation.

For moving surfaces, one can try to reduce wear by:

- Minimising the potential for wear by avoiding the conditions which lead to it, such as contact between vibrating surfaces
- Selecting materials and surface treatments that are wear-resistant or self-lubricating
- Designing efficient lubrication systems and ease of access for lubrication

However, in most electronic cases, direct lubrication in the sense of adding oils is not a possibility, not least because most lubricants are both non-conducting and inhibit solder wetting!

Typically one seeks to avoid surfaces coming into contact, and tries to limit the extent of rubbing motions. For example, many connectors are made on a 'Zero Insertion Force' (ZIF) principle, where the pressure that creates the contact is made only once the connecting parts have been inserted fully. Care is also taken to select suitable surface finishes, and to ensure that the surfaces are of sufficient and equal hardness.

Author: Martin Tarr