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Solid state spreading in the Cu/Cu system

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Solid state spreading of copper particles on a copper polycrystalline substrate was analysed at 1050°C. A specific procedure was settled to produce pure monocrystalline and nearly spherical copper particles. Spreading dynamics were analysed from SEM images and preferential particle/substrate orientations were identified by EBSD. The effect of a preferential orientation on the spreading kinetics is limited, if any. A general agreement is found between the kinetic results and numerical calculations of Mullins [1] for mass transport by surface diffusion under the action of surface curvature gradients. The experimental kinetics are however significantly more rapid, due to the contribution of other mechanisms like volume diffusion.

1. Introduction

Solid state spreading and infiltration of a refractory phase by a metal can play an important role in processing of composite materials (W-Cu, W-Ni-Fe, WC-Co, ...) through powder metallurgy, especially for a particle size being very small (0.1–10 μm) [2]. This work is a part of a research program which aims to analyse and understand the mechanisms of such processes at the micronic scale.

Much experimental work in the literature on solid state spreading is dedicated to the analysis of equilibrium conditions [3–9]. An interesting difference with the wetting by a liquid is the trend for preferential orientations between the spreading particle and substrate, to reduce the interfacial energy [7, 8].

But very few experimental results deal with the dynamics of solid state spreading of micronic particles on a substrate. Experiments of Kuczynski concerning the sintering of spherical particles on a Cu substrate approach this goal [10]. But only the beginning of spreading was analysed by Kuczynski, up to a contact radius 0.5–0.6 times the sphere radius. And copper particles used in this work were obtained from a commercial powder. The observed particles often were polycrystalline and they may contain impurities resulting from powder synthesis.

The aim of the present work is to analyse the mechanisms and kinetics of solid state spreading of Cu spherical particles on a Cu substrate, from the beginning up to nearly complete spreading, and with a control of particle morphology, chemical purity and crystallography. The kinetics will be compared to the numerical calculations of Mullins [1].

2. Mullins calculations of spreading kinetics

Mullins [1] has performed a numerical calculation of the particle profile variation in case of solid state spreading of a sphere onto a plane. The surface tension is assumed isotropic and morphological changes only result from mass transport by surface diffusion under the action of surface curvature gradients. Variation of the surface curvature is assumed continuous along the neck surface, which corresponds either to the case where there is no grain boundary (amorphous materials) or to the case where the dihedral angle ψ_e equals 180°. The extent to which the deviation from these conditions can affect the result is not known. The calculations give the profile as a function of a dimensionless time τ:

$$\tau = 10^{-20} \frac{D_S \delta_S \gamma\ \Omega}{kT(2R)^4} t \tag{1}$$

where δ_S is the width of the surface diffusion layer, D_S is the surface diffusion coefficient, γ the surface tension, Ω the atomic volume, k the Boltzmann constant, T the temperature, R the sphere radius and t the time.

Results in the present paper will be compared to Mullins calculations by plotting morphological parameters as a function of the dimensionless time τ. Interest of such a representation is that it can mix results from different annealing times, different annealing temperatures and different particle radii. Indeed, dividing the particle size by a factor of 2 is equivalent to multiplying the time by a factor of 16 according to the model. The whole heating schedule in our experiments was taken into account by calculating an integrated dimensionless time $\int d\tau$ from Equation 1.

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3. Experiments

3.1. Sample processing

Copper substrates were processed from Cu (99.999%) pellets laminated at 50 to 75% strain, polished and annealed at 1050°C in a metallic furnace during 4 h under He/H_2 atmosphere. A polycrystalline microstructure with grain sizes in the range 100–1000 μm and average surface roughness R_a of individual grains about 10 nm was obtained.

A preliminary study of spreading of copper particles from a commercial powder have shown the disastrous effect of powder impurities on particle spreading. This method was then abandoned and a specific procedure was settled to produce pure monocrystalline and nearly spherical copper particles. Polished vitreous carbon substrates ($R_\mathrm{a} = 4$ nm) were annealed at 1150°C for 1 h under vacuum ($P \approx 10^{-4}$ Pa). A 300 nm copper film was then deposited on the substrate by evaporation in ultra-high vacuum inside a molecular beam epitaxy plant. The film was then destabilised by annealing a few minutes at 1100°C in the furnace under He atmosphere. Destabilisation of the film produced nearly spherical particles, truncated with a flat surface at the contact with the substrate (Fig. 1). Particles are then transferred from the carbon to the copper substrate by approaching both substrates in isopropanol medium and applying an ultrasonic vibration. The transfer is favoured by the small contact area of the particles and by the low Cu/C_v adhesion energy. Particles fall on the copper substrate either with a contact on their flat surface, or with a point contact. These configurations will be referred to as "initial surface contact" or "initial point contact" in the following.

Cu/Cu solid state spreading was analysed by annealing different specimens at 1050°C under He/H_2 atmosphere for different times. Samples were first heated at 500°C for 1 h, to reduce the oxide layer at the substrate and particle surface, and then up to 1050°C for different times. The thermal homogeneous area in the furnace is about 10 cm wide and the temperature is checked by a thermocouple located 2–3 cm far from the sample. The precision on the displayed temperature under He/H_2 atmosphere is then better that 5°C. A wetting experiment of a millimetric size droplet of Pb (99.9999%) on the copper substrate was performed in He/H_2 to check that reducing conditions for copper are efficient during our experiments. The measured wetting angle at 700°C was 20° ± 2, as expected for the clean deoxidised Pb/Cu system [11], which testifies an efficient deoxidisation and an oxygen partial pressure lower than 10^{-19} Pa.

3.2. Characterisation techniques

SEM (JEOL 840A) was used to observe the copper particles resulting from the film destabilisation on the carbon substrate. The particle size distribution was analysed from images at normal incidence. Side views with 5° incidence were also performed to analyse particle shapes, and to measure the Cu/C_v wetting angle and contact radius.

Cu/Cu particle spreading was also analysed from SEM side views with 5° incidence. Particle contour co-ordinates were extracted through image processing and different morphological parameters were systematically computed (Fig. 2). Specific image processing codes and parameter calculations were developed using the Aphelion image analysis software (ADCIS S.A.).

Electron backscattering diffraction (EBSD) was used (TSL device with OIM software) to analyse possible particle/substrate preferential orientations.

4. Results

4.1. Initial particle morphology

The shape of particles on the carbon substrate is nearly spherical. Small facets are observed on the surface that are formed during cooling after destabilisation. But the general shape is that of the liquid droplets at 1100°C, i.e. truncated spheres with a flat surface at the contact with the substrate (Fig. 1), and with a wetting angle in the range 130–140°, in agreement with literature [12]. The ratio $x_\mathrm{C}/x_\mathrm{max}$ of the contact radius to the particle radius is about 0.7 and particle diameters lie in the range 5–20 μm.

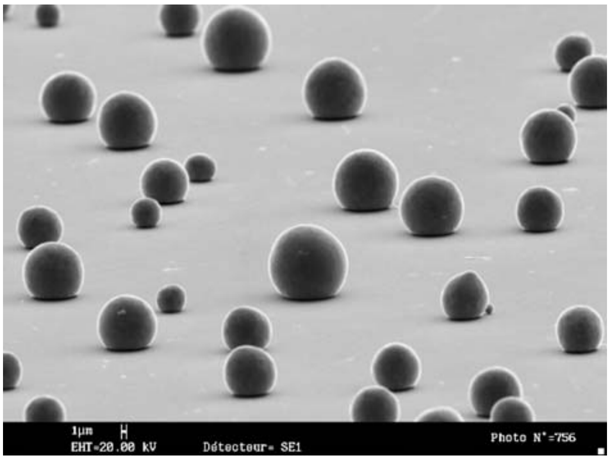


Figure 1 Cu particles on a vitreous carbon substrate, resulting from the destabilisation of a Cu film.

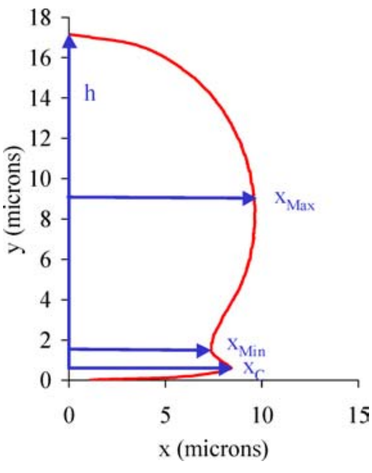


Figure 2 Average particle semi-profile and representation of morphological parameters obtained from image analysis (the initial sphere radius is deduced from the computed particle volume).

Figure 3 Different stages of Cu/Cu particle spreading.

4.2. Cu/Cu spreading

Fig. 3 presents different stages of particle spreading at 1050°C. A hollow is observed around particles, a concave neck is formed at the contact between particles and substrate and the global profiles are similar to those calculated by Mullins. Variation of the profile at a given temperature is a function of time and of the initial particle size. A grain boundary is systematically observed between the particle and the substrate at the beginning of spreading. This grain boundary is parallel to the substrate plane or sometimes slightly tilted ($<$15–20°) and it migrates to the top of the particle in the late stage of spreading (Fig. 4). Discontinuity in the particle surface curvature at the grain boundary tip is hardly detectable on the images (Fig. 4), which means that the dihedral angle is not far from 180° in any case. Indeed, the dihedral angle of general grain boundaries of copper at temperature near to the melting point is as high as 160° (see for example [13]). This value could even be higher for low-energy grain boundaries.

Relative orientations between particles and the substrate were analysed by EBSD after spreading at 1050°C. Particles with initial surface contact do not present any preferential orientation at $t = 0$ h. To the contrary, most particles with initial point contact have a coincidence relation with the substrate lattice at $t = 0$ h (Table I). After 3 h at 1050°C, most particles are in epitaxy with the substrate, due to the grain boundary migration.

The morphological parameters measured on the profiles are plotted versus the dimensionless time τ on Fig. 5, together with Mullins calculations and with the previous experimental results of Kuczynski [10]. Dimensionless time τ is calculated using the value $\gamma = 1.6$ J/m^2 for the surface tension [11]. δ_S and D_S values are those taken by Mullins: $\delta_S = 0.26$ nm and D_S values are a compilation of data from sintering, thermal grooving and scratch smoothing techniques and yield a pre-exponential factor $D_0 = 0.0214$ m^2/s and activation energy $Q = 161$ kJ/mol [1]. Particles with initial surface contact are integrated in the plot by adding to the calculated dimensionless time τ the calculated dimensionless time τ_0 necessary to achieve a contact radius 0.7 R_0 (radius of the initial surface of contact). This additional time is simply represented as an error bar for all points of samples heated 3 h at 1050°C, since the flat surface is no more visible after so much spreading. There is no noticeable difference on the global kinetic behaviour of particles with an initial point contact or surface contact.

TABLE I A few special boundaries with coincidence site lattices identified between particles and the substrate for particles with initial point contact (1050°C, $t = 0$ h)

CSL ($\pm$2.5)	Axis	Number of particles
$\Sigma 3$	[1 1 1]	4
$\Sigma 9$	[1 1 0]	2
$\Sigma 11$	[1 1 0]	1

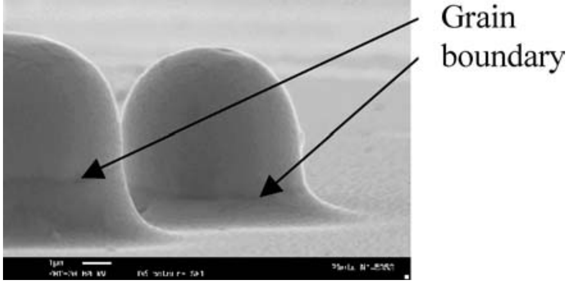
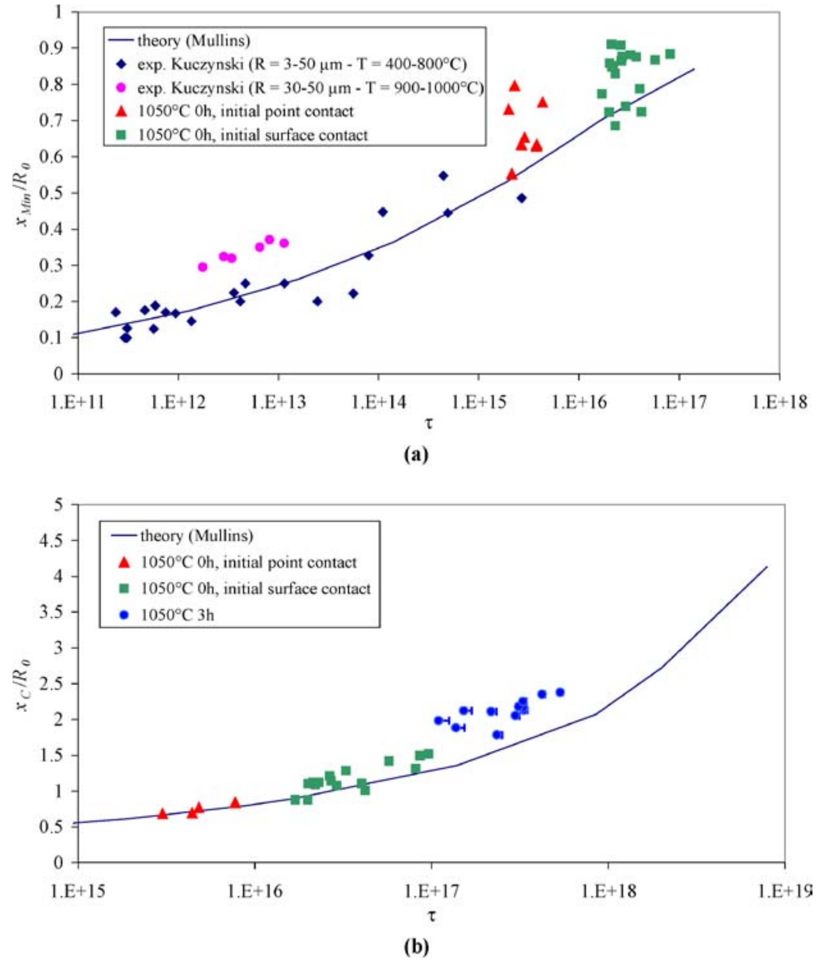


Figure 4 Cu particle on Cu substrate showing the initiation of grain boundary migration as soon as the grain boundary can move without increasing its area.

5. Discussion

The present study analyses Cu particle spreading on a Cu planar substrate. It extends the previous experimental work of Kuczynski to much higher spreading ratio x_C/R_0 (x_C/R_0 up to 2.5 instead of 0.5–0.6 in Kuczynski experiments, see Fig. 5) with a better control of particle shape, chemical purity and crystallography. The different steps of solid state spreading may be summarised as follows (Fig. 6), in agreement with our observations.

As soon as a grain boundary form at the particle/substrate contact, rapid local matter redistribution occurs to ensure equilibrium dihedral angle (Figs. 6a and b). Neck growth results from mass transport to the concave neck (Fig. 6b and c) until complete spreading (Fig. 6d). The grain boundary migrates to the top of the particle in the late stage (Fig. 6c), as soon as it is no more anchored by the concave neck, i.e. when it can move without increasing its area. In addition, special grain boundaries may form at the initial point contacts. This was already observed for Cu/Cu particle spreading but on surfaces parallel to low index planes [14]. In our case where the substrate grains have no special orientations, particles must rotate to find a coincidence lattice with the substrate and the grain boundary plane may



(a)

(b)

Figure 5 Variation of the dimensionless particle neck radius $x_{\min}/R_0$ (a) and of the dimensionless particle-substrate contact radius x_C/R_0 (b) as a function of the dimensionless time τ. (Kuczinsky only measured the neck radius $x_{\min}$ at the beginning of spreading, i.e. in conditions where $x_C \approx x_{\min}$, and for $x_{\min}/R_0$ values lower than 0.5–0.6).

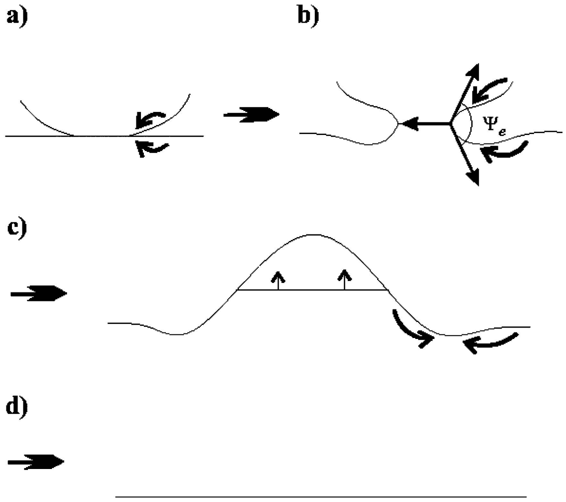


Figure 6 The different steps of solid state spreading of a sphere onto a plane.

tilt to find a lower interfacial energy. Grain boundary tilting proceeds from reducing the interfacial energy of the grain boundary without increasing its area too much and the tilt angle remains relatively low.

The global trend of spreading kinetics is consistent with experiments of Kuczynski, and with numerical calculations of Mullins for curvature driven surface diffusion. Spreading is however more rapid than predicted by the calculations both in our case and in Kuczynski experiments at 900–1000°C. This may be due to a contribution of mechanisms with higher activation energy at high temperature, such as volume diffusion, as already considered by Kuczynski. Indeed the ratio of volume diffusion to surface diffusion neck growth rate in Kuczynski model for the initial stage of sintering is:

$$\frac{(\dot{x}_{\min}/R_0)_{\text{v.d.}}}{(\dot{x}_{\min}/R_0)_{\text{s.d}}} = \frac{D_V}{\delta_S D_S} R_0 \, (x_{\min}/R_0)^2 \tag{2}$$

This ratio increases with the particle size, the degree of spreading and the temperature. It is about 16% at 1050°C for particles with radius $R_0 = 6$ μm and for $x_{\min}/R_0 = 1$, which means a significant contribution of volume diffusion to mass transport. Grain boundary diffusion and vapour transport may in addition play a role.

Scattering of our spreading data for the same dimensionless time τ (i.e. for the same particle size at fixed T and t) is another issue of the results. It is about 0.2 R_0 for $x_{\min}$ or x_C, which is much larger than the experimental error on the measurement of these distances. This scattering is apparently not an effect of the preferential orientation since it was checked that the degree of spreading is not significantly higher or lower for particles having a coincidence lattice with the substrate than for arbitrary oriented particles. And similar scattering is observed for particles with initial surface contact, which do not have a coincidence lattice with the substrate, than for particles with initial point contact. The influence of a preferential orientation on spreading could be complex since different effects could compete: (i) the dynamic interference between mass transport driven by reduction of interfacial energy (particle and grain boundary rotation) and by surface curvature; (ii) the effect of grain boundary energy on the dihedral angle which in turn may influence surface curvature ; (iii) the effect of grain boundary structure on the grain boundary diffusivity. Other effect, like surface impurities or local fluctuation in the surface roughness may account for scattering of the data.

6. Conclusion

Solid state spreading of copper spherical particles on a copper polycrystalline substrate was analysed at 1050°C. The morphological variation is consistent with a mechanism of surface curvature driven mass transport. Preferential orientations between particles and substrate were identified but their effect on spreading kinetics is limited, if any. The general trend of morphological variations is correctly described by the model of Mullins [1] which is based on a mechanism of mass transport by surface diffusion under the action of surface curvature gradients. The experimental kinetics are however significantly more rapid, due to the contribution of other mechanisms like volume diffusion. The more general case of solid state spreading in a system with partial wetting will be studied in the future with the Cu/W couple.

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