JOURNAL OF MATERIALS SCIENCE 9 (1974) 1955–1960

Sintering, fracture and oxide films

P. J. HEATH, P. E. EVANS
Department of Metallurgy, The University of Manchester Institute of Science and Technology, Manchester, UK

Observations of fractured necks in sintered copper powders show that a homogeneous bond is not obtained across the whole neck diameter. A neutral atmosphere produces a central region which fails in a ductile manner and a surrounding annulus which fails in a brittle manner. The presence of an oxide film on the particles is considered to be the cause and the present work shows that under certain conditions, the assumption made by many authors that the neck is homogeneous across its width, is incorrect.

1. Introduction

Atomistic processes in materials are often represented by greatly simplified models. This is a necessary first step but where the mechanism is based on experimental results obtained under one set of conditions it is dangerous to invoke the same mechanism to account for results obtained under different conditions. Many wrong directions have been taken in this way.

The sintering of metal powders is no exception and theories of the early stages of sintering have concentrated on the kinetics of neck growth on the assumption that the neck region is homogenous. Whereas this is usually true for sintering in a reducing atmosphere it is not generally true for sintering in a neutral atmosphere.

The phenomenon and kinetics of the sintering process have been examined at great length by the use of simple models. Sphere–sphere, sphere–plate, wire wound bobbin and twisted wire systems have all proved enlightening and measurements of neck widths with increasing sintering times have given an insight into the mechanisms operating. Thümmler and Thomma [1] have made a comprehensive review of the published work on the sintering process.

To the best of our knowledge, the only previous work on fracture surfaces of sintered necks is that by Gwathmey and Dyer [2]. They brought orientated single crystal spheres of copper into contact at sintering temperatures for various lengths of time. These were then pulled apart and allowed to cool to room temperature. The fracture surfaces showed a fingering effect which was thought to be due to the anisotropy of surface energy. Special care was taken to ensure that the surfaces were free from contamination but no experiments were made on oxidized surfaces at high temperatures.

The effects on the mechanical properties of compacts made from powders having an oxide film have been studied by Clasing [3] and by Ramakrishnan and Tendolkar [4, 5]. They plotted tensile strengths of specimens sintered under fixed conditions, against surface oxide thickness on the powder before sintering and found a peak strength at an oxide thickness of 500 A.U. (for copper). They also found that the strength, for a given oxide thickness, was higher for a material sintered in a reducing hydrogen atmosphere than for sintering in nitrogen or vacuum.

In the present work the material was used as-received, i.e. it possessed a surface oxide film which is the condition most common in commercial practice.

2. Experimental procedure

Essentially spherical, air atomized, copper powder in the size range 124 to 147 μm was poured into a small rectangular specimen boat (approximately 1cm $\times$ 1cm $\times$ 0.5cm) made by folding 0.13 mm thick copper foil. The powder was polycrystalline and the boat was tapped gently to consolidate the powder. The sample was not pressed.

Heating in a nitrogen atmosphere at 850° C for times of 2, 5, 15, 35 and 135 min produced partial sintering of the powder both to itself and to the copper foil. The geometry under which particle–particle and particle–foil necks had been formed was, therefore, equivalent to the

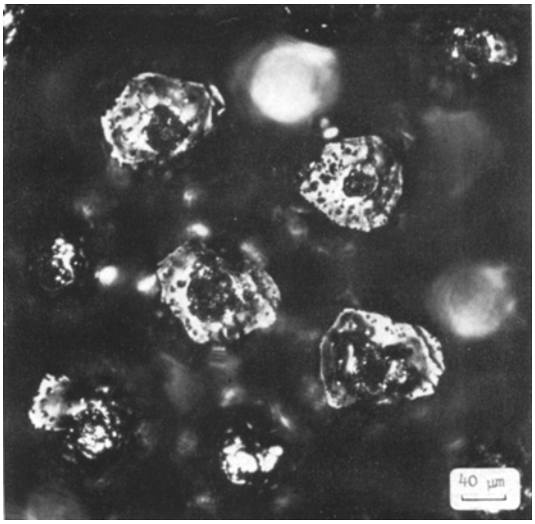

Figure 1 The appearance of the fracture surfaces on particles previously in contact with foil. (Optical micrograph.)

sphere–sphere and sphere–plate models used by previous workers.

By folding away the sides of the specimen boat and peeling the foil from the partially sintered block of copper particles, the particle–foil contact points were broken. Breaking the particle mass itself produced particle–particle fracture spots. The fractures were examined under the optical microscope and in the scanning electron microscope. Some direct carbon replicas were also made for examination in the electron microscope.

3. Results and discussion

The fracture surfaces of the contact spots were examined at low magnifications in the optical microscope. The general appearance (Fig. 1) was that of a rough central region, essentially circular, surrounded by a very bright, i.e. highly reflective and featureless, annulus. Higher magnifications in the scanning electron microscope showed that the central region (Fig. 2) had all the features characteristic of ductile failure. On the other hand, the smooth relatively featureless surface of the annulus was consistent with that produced by a brittle fracture. Although this type of dual fracture surface was the norm, a few, particularly from those specimens sintered for only a short time (2 and 5 min), showed only a ductile fracture region. A few similar spots, i.e. showing a ductile central region only, were found in specimens sintered for the longer times. These were usually small in size and it was concluded, therefore, that these were relatively new contact areas formed as a result of repacking of the particle mass. Only on very rare occasions were contact spots seen which did not have a central "ductile region"; the fracture surface then appeared completely brittle across the whole of the contact area.

Surfaces produced by fracture of particle–particle necks gave similar results to those

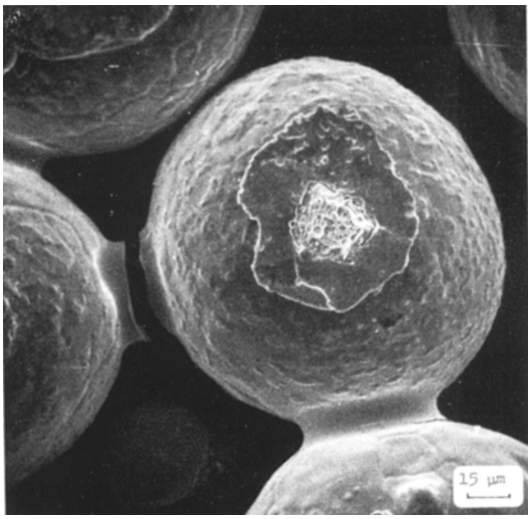

Figure 2 The particle-foil fracture surface and necks between particles. (S.E.M.)

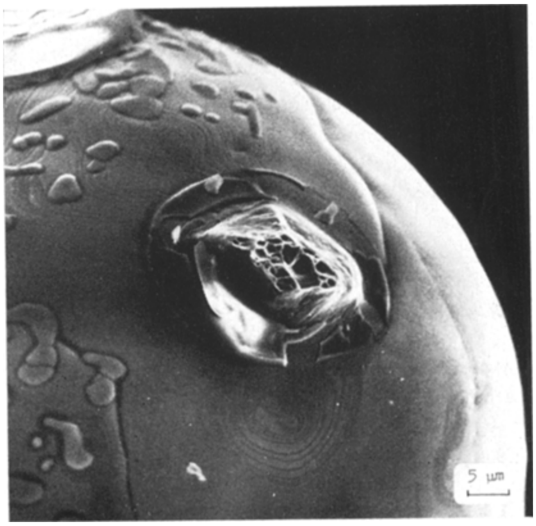

Figure 3 The type of fracture spot produced by failure of a particle-particle neck. (S.E.M.)

Figure 4 Particle-foil neck (taken from foil) showing square edge nature of annulus. (S.E.M.)

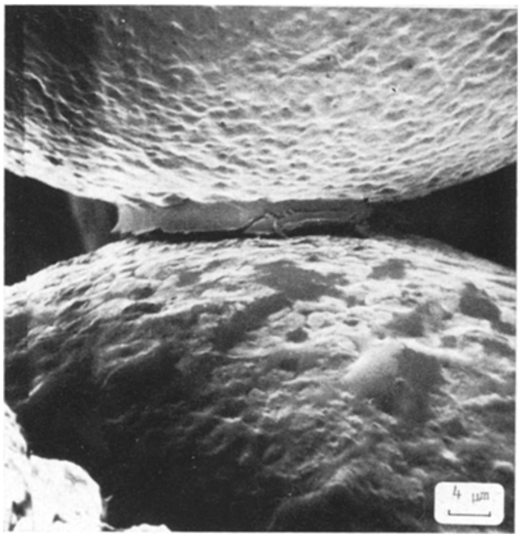

Figure 5 Fractured neck; note absence of any visible plastic deformation. (S.E.M.)

produced from particle–foil necks (Fig. 3). The most noticeable difference was that the annulus regions were "rougher" than those in particle–foil junctions. This is probably due to either the different geometry under which the necks had formed or to the foil having slightly different properties from those of the particles. Indeed, the tendency for many of the annuli of particle–foil spots to have "square" edges (Fig. 4) suggests the influence of the cube texture of the foil. The central weld spot, however, always remained essentially circular.

Failure of the neck usually took place along a sphere–neck (or foil–neck) boundary, rather than across the smallest, most highly stressed cross-section at the centre of the neck. Where partially fractured necks were seen it appeared that the fracture crack had begun at the particle–neck interface. In Fig. 2 a crack is visible in the particle–particle neck in the lower right hand corner. It is believed that in some cases the crack may propagate around the annulus in a helical fashion. This can account for the observed step line in the annulus of the particle–foil fracture surface, also shown in Fig. 2. Fig. 5 shows the other common mode of failure: the fracture takes place along the neck particle interface. This mode

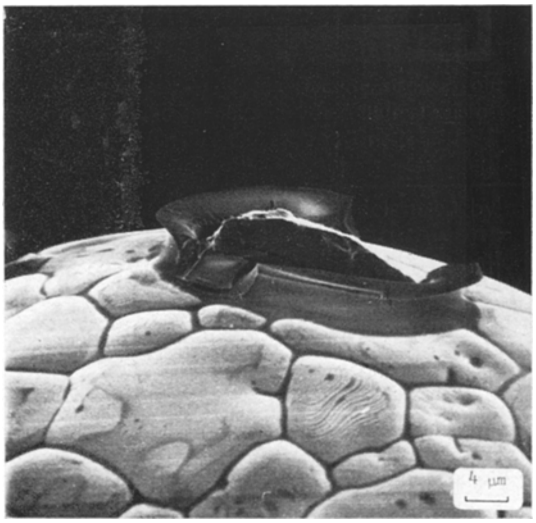

Figure 6 Particle-particle neck. (S.E.M.)

is strikingly shown in Fig. 6 where the annulus of the neck has a shape consistent with that of the removed spherical particle. In Figs. 5 and 6 the brittle nature of the fracture in the annular region is particularly evident.

The pronounced thermal etching of the particle surface and the absence of it in the neck region is also clearly shown in Fig. 6. At higher resolution, from direct carbon replicas, the external surface of the neck (Fig. 7) still appears very smooth and uniform. The edges of the neck can be seen to give way quite sharply to the thermally etched surfaces of the parent particles. The "undercut" reported by other workers [6], is not evident. Fig. 8 is a replica of a particle–foil fracture spot taken from the particle. The annulus shows striations consistent with brittle

Figure 7 Direct carbon replica of neck between two particles.

Figure 8 Direct carbon replica of particle-foil fracture surface, taken from particle surface.

fracture and the central region the ductile failure characteristics of dimples and "serpentine glide" [7]. The black ring around the annulus is a result of the inflexion of the neck, the electron beam is unable to penetrate the triple carbon layer.

Attempts were made to obtain a cross-section of a particle–particle neck but the perfect curves of necks seen in the scanning electron microscope were never realized in section. Random sections through a plasticine model in which the neck was of a different colour showed some of the possible configurations which would be (and were) observed in the microscope. Only when the centres of the two particles lie in the plane of the section does the section show the true curve of the neck.

By using an optical microscope fitted with a graduated eyepiece the rate of growth of the *central* weld region was found to follow an equation of the form $w = kt^{1/3.25}$, where w = central weld radius, k = numerical constant and t = time. This should not be confused with the time dependence of the *total* neck radius, which is what has been measured by other workers.

Our interpretation of these observations is that the dual nature of the fracture surface of necks is a result of the oxide film on each particle coupled with the non-reducing sintering atmosphere used. Since the powder was used as-received, the contact condition prior to sintering may be represented as shown in Fig. 9a; the particles have a thin oxide film around them. As sintering proceeds (diffusion of copper taking place through the oxide layer) the neck region is built up and the engulfed oxide film breaks up into the thermodynamically stable state of discrete particles. This process will be diffusion controlled and one would expect some time lag between the oxide film being covered by the advancing neck front and its breaking into discrete particles. It would follow that the continuous oxide film on the particles extends some way into the neck, while the central region, having been in existence for a longer time, will contain a dispersion of oxide particles

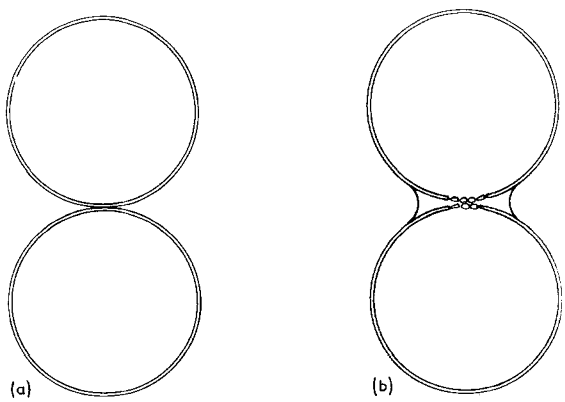

Figure 9 Schematic representation of (a) contact condition before sintering and (b) after some neck growth has taken place.

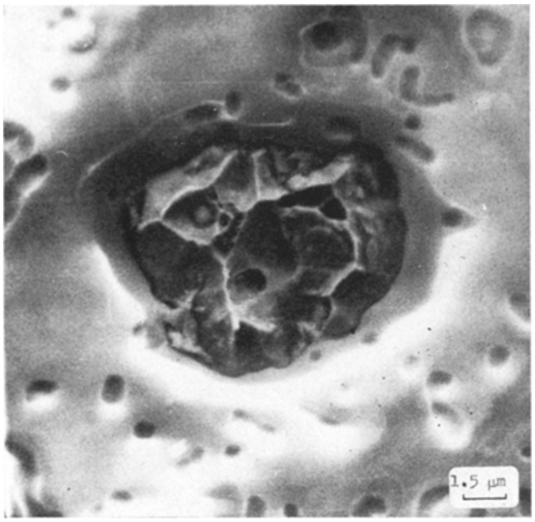

Figure 10 Particles in dimples of central ductile region. (S.E.M.)

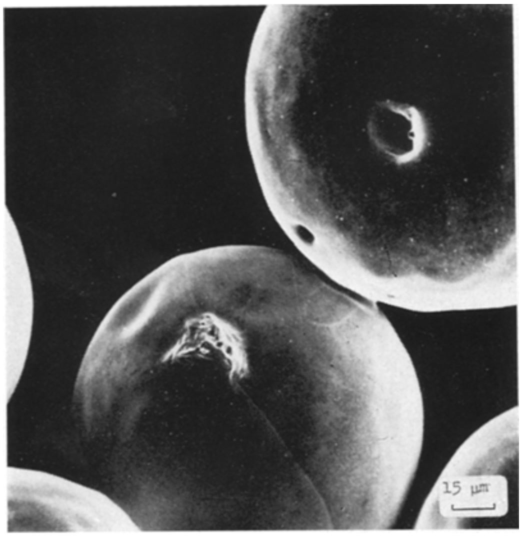

Figure 11 The type of particle-particle fracture spot produced by sintering in hydrogen for 2 h. (S.E.M.)

(Fig. 9b). Breaking such a contact would result in the observed fracture characteristics: the relatively weak neck–oxide interface in the outer section of the neck fails in a brittle manner and the central region fails in a ductile manner, wherein void formation, assisted by the presence of oxide particles, is followed by coalescence. In Fig. 10 these particles can be seen clearly, sitting at the bottom of the dimples in the ductile fracture region. One implication of the presence of an oxide film on the particles is that one would expect an "incubation period" for the commencement of sintering i.e. the time taken for copper atoms to diffuse through the oxide film. Although no systematic measurements have yet been made, it was found that the particles did not adhere to one another until sintering had taken place for at least 2 min.

Additional evidence for the mechanisms postulated above was obtained by sintering specimens in a hydrogen atmosphere. Under these conditions no brittle annulus was observed. The reducing conditions removed the oxide layer and the interparticle neck failed by ductile fracture over the whole neck diameter. Fig. 11 shows the type of fracture spot produced by sintering in hydrogen, note the absence of oxide particles. Further evidence was obtained from specimens pressed at 386 $MN\,m^{-2}$ and sintered in a nitrogen atmosphere. The pressing operation, apart from producing a larger contact area also breaks up the oxide film into separate particles. The changed geometry around the contact region, produced by the pressing operation, results in only a small increase in the diameter of the neck, compared to that produced by sintering unpressed powder for a similar time. The annulus region produced on fracture is, therefore, quite small (see Fig. 12).

We have considered other mechanisms but none is able to explain all the observed effects. It was noted that specimens sintered in hydrogen

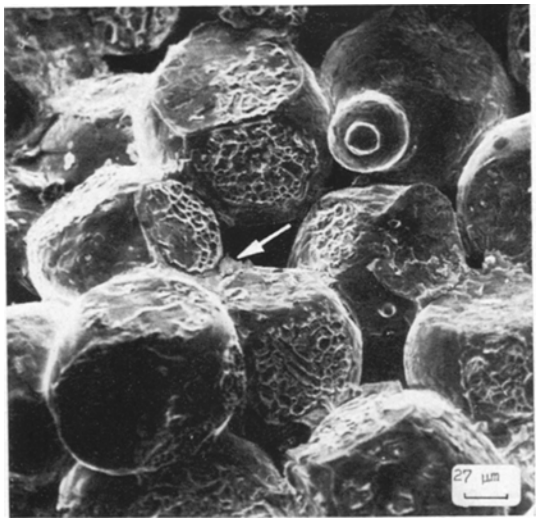

Figure 12 Fracture surfaces between particles produced by pressing at 386 $MN\,m^{-2}$ and sintering for 2 h in nitrogen. Note limited annulus region (arrowed). (S.E.M.)

were stronger than specimens sintered in nitrogen. This is consistent with the work of Ramakrishnan and Tendolkar [5]. Since the neck produced by sintering in nitrogen is inherently brittle, for the reasons deduced above, it is suggested that sintering in hydrogen does not *increase* the tensile strength of the compact but rather that sintering in nitrogen effectively *decreases* it. A 2 h sintering period in a nitrogen atmosphere produced central ductile weld regions with an average diameter of 35 μm, whilst sintering for 2 h in a hydrogen atmosphere gave a ductile weld spot of approximately 23 μm. The smaller (hydrogen) junctions were stronger since, after sintering in nitrogen, particles of oxide were left in the contact region when the initially continuous oxide film broke down and provided easy sites for the nucleation of voids and subsequent ductile fracture.

4. Conclusions

(1) When copper spheres, with a surface oxide film are sintered in nitrogen, junctions are formed that show two distinct types of surface on fracture: (i) a central region that has failed in a ductile manner, (ii) a surrounding annulus that has failed in a brittle manner.

(2) The junction formed by sintering in nitrogen is inherently weak because the oxide film extending into the neck region is brittle and cracks, thus introducing a stress concentration.

(3) Junctions sintered in hydrogen show a ductile fracture surface only, which is stronger per unit size than a nitrogen sintered junction.

To summarize, therefore, particles having surface oxide films produce weak junctions upon sintering unless a reducing atmosphere is used, i.e. oxidized particles give weaker compacts, at least in the early stages of sintering.

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Received 18 March and accepted 17 April 1974