
A process for sintering submicron silver powders is described. The process allows for a reasonable surface area (determined by the BET adsorption isotherm technique) whilst maintaining a strong mechanical contact between the sinter and silver foils or silver plated copper plates.

A recipe for sintering submicron silver powders

V. Keith and M.G. Ward

Key words: cryogenics, sintering, submicron silver

Cooling liquid helium to very low temperatures is made difficult by the very poor Kapitza boundary conductance between liquid helium and a solid surface. In consequence thermal contact to the helium is invariably made by using a very large surface area of contact either by using powdered refrigerants directly or sintered metal powder pads. In the latter context silver powders have been widely used since submicron silver powder is readily available, does not oxidise readily and is very easy to sinter. Since the final temperature of the helium sample depends only on the ratio of the surface area to the heat leak it is important to make the area as large as possible. To assist the design of our own refrigerator¹ we have made measurements on the surface area of submicron silver powders and the resulting sinters. In the literature²⁻⁵ reported areas vary widely depending on the sintering process. In this note we report results showing the effect of varying a number of the conditions in order to obtain the optimum process for sintering submicron silver powders.

We used the BET adsorption isotherm technique^{6,7} for measuring the surface area using argon as the adsorbate at 77 K. The volume at which the volume-pressure curve becomes linear (point B method) was determined and converted into a surface area by multiplying the volume by $3.37 \text{ m}^2 \text{ cm}^{-3}$. The first interesting results obtained were on the silver powders in the 'as received from manufacturers' condition. Table 1 shows the areas/g of the three different silver powders measured, namely the nominally 40 and 70 nm Japanese powders from Vacuum Metallurgical Co Ltd, Tokyo and 700 nm French powder from Comptoir Lyon-Alemand, Louvout, Paris. The French powder has a rather low surface area, $0.2 \text{ m}^2 \text{ g}^{-1}$, while the two Japanese powders give approximately the same surface areas of $1.5 \text{ m}^2 \text{ g}^{-1}$. The similar surface areas obtained for the 40 nm and 70 nm Japanese powders suggest that the average particle size in the two powders is the same. The measured surface areas are much smaller than the values calculated for spheres of the quoted size, see Table 1. The '40 nm' Japanese silver powder is the worst case, the measured surface area being almost ten times smaller than the calculated value of $14 \text{ m}^2 \text{ g}^{-1}$. Our batches of the nominally 40 nm and 70 nm silver powders yield surface areas smaller than those reported by other workers. Frossati² for example quotes typical specific areas after sintering of $1.8 \text{ m}^2 \text{ g}^{-1}$ for 70 nm powder and $2.2 \text{ m}^2 \text{ g}^{-1}$ for 40 nm powder. The only conclusion that we can draw from these results is that there must be a large variation in the average particle size from batch to batch.

The surface area was also observed to decrease as a function of time. The '70 nm' Japanese silver powder remeasured after storage at room temperature for six months in air showed an approximately 35% reduction in surface area. The '40 nm' silver powder showed a similar rate of reduction in surface area after storage under similar conditions for three months. This reduction in surface area suggests that a self-sintering process takes place at room temperature.⁵ The surface areas of the Japanese silver powders could be increased again to their 'as received from manufacturers' value by a gentle presintering treatment which consisted of warming the powders on the hot plate of a heated desiccator at 50°C in hydrogen at atmospheric pressure. No improvement in the surface area of the '40 nm' silver powder was observed when the presintering temperature was 25°C and the surface area decreased when the presintering temperature was increased to 100°C suggesting a small temperature range around 50°C for presintering.

When the powders were compressed by applying a pressure of $75 \times 10^6 \text{ N m}^{-2}$ the surface area decreased by only a few percent but if the pressure was increased to $150 \times 10^6 \text{ N m}^{-2}$ the surface area decreased by approximately 50%. Further reduction of the surface area resulted on warming the compressed samples as shown in Fig. 1.

With this information in hand we developed our recipe for sintering silver powders on to annealed silver foils or silver plated copper plates. The silver foils were first scored and perforated and then spot welded to flattened 1 mm diameter silver wire to make external thermal contact. The Japanese silver powder was presintered at 50°C in hydrogen at atmospheric pressure on a hot plate for one hour. The presintered powder was then compressed to $75 \times 10^6 \text{ N m}^{-2}$ in a hand press with a prepared silver foil sandwiched in the centre. The compressed powder and foil sandwich was then clamped in a jig (the bolts on the jig were tightened with a torque wrench to 300 cm kg) and heated to 200°C in hydrogen at atmospheric pressure on the hot plate of the dessicator for 12 min. The resulting surface area was $0.8 \text{ m}^2 \text{ g}^{-1}$ of silver powder. It is possible to sinter at a lower temperature but the mechanical contact between the silver foil and the sinter becomes poorer and little is gained in surface area until the sintering temperature is much lower as shown in Fig. 1. The strength of the mechanical contact between the foil and sinter (determined by breaking the sinter away from the foil) can be improved by dusting the silver foil with a very small trace of the 700 nm French silver powder.⁸ The quantity of French powder used is critical since 0.5 g of

Table 1. The surface areas measured after the prescribed treatment for three submicron silver powders

Treatment	Surface area $\text{m}^2 \text{g}^{-1}$		
	Japanese 40 nm Ag	Japanese 70 nm Ag	French 700 nm Ag
Powder in 'as received' condition	1.5	1.63	0.2
Powder remeasured after storage for several months in air at room temperature	1.26 (3 months)	1.04 (6 months)	
Powder unsintered, compressed to $75 \times 10^6 \text{ N m}^{-2}$		1.59	
Powder unsintered, compressed to $150 \times 10^6 \text{ N m}^{-2}$	0.8		
Presintered for 1 h in H_2 at atmospheric pressure and 25°C	1.07		
Presintered as above at 50°C	1.4	1.5	0.37
Presintered as above at 100°C	1.06		
Powder compressed to $75 \times 10^6 \text{ N m}^{-2}$ and sintered at 40°C in hydrogen at atmospheric pressure		1.19	
As above but sintered at 75°C		1.07	
As above but sintered at 100°C		0.94	
As above but sintered at 200°C		0.83	
Surface area calculated from quoted nominal particle size	[14]	[8]	[0.8]

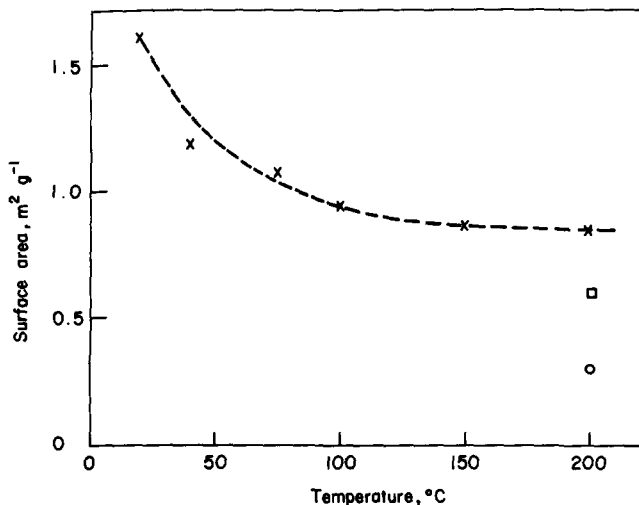


Fig. 1 The surface area of the 70 nm Japanese silver powder compressed to 75 N m^{-2} and sintered in hydrogen at atmospheric pressure for 12 min as a function of temperature. The graph also shows the effect on the surface area of the sinters of introducing small quantities of the 700 nm French silver powder into the sintering process. (X - no Fr Ag powder; □ - dusting of Fr Ag powder; and ○ - 30% Fr Ag powder)

French powder laid under 1 g of 70 nm Japanese silver powder will result in a final surface area of $0.3 \text{ m}^2 \text{g}^{-1}$ instead of $0.6 \text{ m}^2 \text{g}^{-1}$ expected from the composite. Even a dusting of the French powder results in a 25% decrease in the surface area. This apparent poisoning of the surface area may be due to some form of coating (eg grease) on the French silver powder. We tried to remove the coating by degreasing the powder in acetone followed by separation in a centrifuge and drying on a hot plate at a temperature just above room

temperature. The surface area of the French powder remained the same and the resulting sinters showed no improvement in the total surface area.

In summary, we have chosen a compromise recipe for sintering submicron silver powders. The recipe allows for a reasonable resultant surface area whilst maintaining a strong mechanical contact between the sinter and the foils or copper plates.

Authors

The authors are from the Department of Physics, University of Lancaster, UK. Paper received 19 September 1983.

We would like to thank our collaborators A.M. Guénault and G.R. Pickett for many useful discussions.

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