mechanism for sintering. It also seems to be borne out by the fact that long periods of annealing at temperatures similar to those which give significant changes in surface structure for short periods do not improve the surface structure further. Assuming that the bulk has an effect on the surface layers, either volume diffusion is so small that the bulk changes very little and consequently the surface is constrained so that it cannot improve any further; or alternatively volume diffusion is significant, in which case the change is only comparable with the initial surface improvement which nucleates and grows on the bulk as a substrate These results do not seem inconsistent with the results of Cho [4] on GaAs, for in the work reported here ZnS evaporated to such an extent that eventual layers were of similar thickness to those examined by Cho. It seems evident therefore that in both instances significant improvement in crystal structure only occurred when the layers were so thin and the temperature such that surface diffusion could be significant, and when the structure some tens of monolayers below the surface was of good quality and did not constrain the surface layers, but allowed them to nucleate and grow. It seems likely that this may be generally the case and annealing results which give epitaxy can only occur where surface mobility effects have a dominant role as in very thin films.

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Received 15 March
and accepted 23 April 1971

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The Thermal Conductivity of Porous Copper

Increasing use is being made of powder metallurgical techniques to fabricate components, but information on the thermal conductivity of porous metals is still sparse. Grootenhuis *et al* [1] demonstrated that the thermal and electrical conductivities of porous bronze compacts both decrease linearly with increasing porosity, reaching notionally zero values at a porosity of 47.64%; this is the theoretical porosity $[100(1 - \pi/6)]$ of a simple cubic array of touching uniform spheres, and is independent of radius. Literature data for the electrical conductivity of porous copper, iron and nickel compacts are found to lie on the same linear plot. Recently, Taubenblat [2] has measured the electrical conductivity of copper sintered at 1000°C and obtained results near this line. The same trend is shown in several Russian papers on sintered iron, nickel and steel [3-6], although porosities up to 55% are quoted, presumably because of the presence of large pores. Similar results have been reported also for porous tungsten compacts [7]. Mitoff [8] in a recent treatment of the properties of heterogeneous systems states that to a first approximation the conductivity of a metal with fraction of pores x is $[1 - (3/2)x]$ times the conductivity of dense metal. Euler [9] has produced a theoretical model which closely resembles the empirical Grootenhuis relationship and considers factors which can lead to a departure from linear behaviour. The Grootenhuis relationship applies to uniform spheres, sintered together in good metallurgical contact, but this is possibly not the situation prevailing for unsintered porous metal layers prepared by flame or plasma-spraying of powders.

In the present letter we report thermal conductivity data for porous copper compacts prepared by these techniques, as well as for dense electroplated copper. Methods employed to prepare sprayed copper have been described in the literature [10]. The thermal conductivities were derived from thermal diffusivity measurements over the temperature range 40 to 600°C according to the relation

$$k = \alpha \rho \, C_p$$

where k = thermal conductivity [watts.m^{-1}K^{-1}], ρ = density of compact [Kg.m^{-3}], α = thermal diffusivity [m^2.sec^{-1}], and C_p = specific heat [joules Kg^{-1}K^{-1}]. Specific heat values for copper, which are independent of porosity, were taken from the data of Touloukian [11].

The experimental equipment employed is described in detail elsewhere [12]. Briefly, a pulse of accelerated electrons is used to heat the front surfaces of a disc (6 mm diameter) of the metal. For copper, the discs employed are normally about 4 mm thick. The transient temperature of the rear face of the specimen is monitored by an intrinsic thermocouple, and the amplified signal displayed on an oscilloscope. From the time taken $(t_{\frac{1}{2}})$ for the rear face to reach half its maximum temperature the thermal diffusivity (α) and hence the thermal conductivity (k) are calculated. The advantages of the diffusivity method over conductivity measurements (small specimen size, absolute temperature differences not required, heat loss problems overcome) are well established.

Measurements were made on 4 mm-thick discs of four different types of copper:

(i) Ordinary copper rod
(density 8.85 × 10^{3}Kg.m^{-3} Porosity 0%)
(ii) Electroplated copper
(density 8.81 × 10^{3}Kg.m^{-3} Porosity 0.5%)
(iii) Flame-sprayed copper
(density 7.42 × 10^{3}Kg.m^{-3} Porosity 16%)
(iv) Plasma-sprayed copper
(density 6.74 × 10^{3}Kg.m^{-3} Porosity 24%)

Thermal conductivity values obtained are plotted in fig. 1 together with the line for the thermal conductivity of bulk copper given by Touloukian [11]. Values obtained for the copper rod and electroplated material are in reasonable agreement with this line. The flame-sprayed material initially gave a very low conductivity, but during heating to 590° C there was a considerable increase which remained on cooling. The room-temperature conductivity of a second disc of this material agreed with initial values for the first disc, but after vacuum-sintering at 800° C for 30 min. the density increased to 7.74 × 10^{3}Kg.m^{-3} and the conductivity was much larger. The material appeared much brighter owing to decomposition of traces of oxide present.

The thermal conductivity of plasma-sprayed copper was still smaller than that of flame-sprayed metal, in accordance with its lower density. On heating to 540° C there was a small increase in k which remained on cooling to room temperature. Sintering at 1000° C gave a further increase in conductivity, but this was considerably less than observed for flame-sprayed copper sintered at only 800° C. A second disc of plasma-sprayed copper had a very low thermal conductivity, presumably due to the presence of a crack or other macro-defect, and sintering at 800° C only increased the room temperature conductivity to 33 watts m^{-1}K^{-1}.

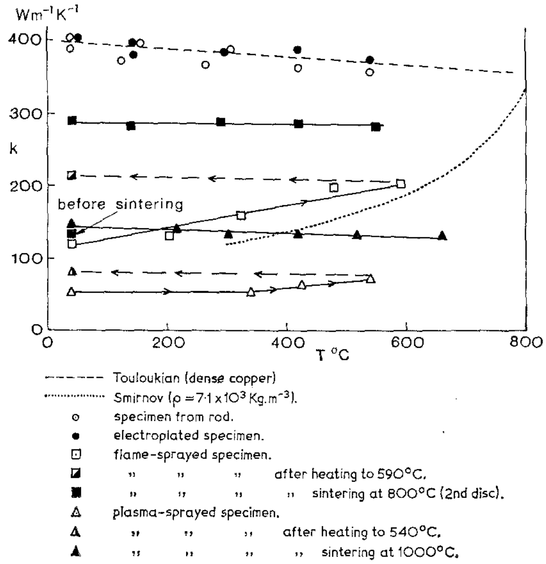

Figure 1 Porous copper: variation of thermal conductivity with temperature.

The conductivities measured at room temperature are plotted against density in fig. 2 and compared to the Grootenhuis relationship (continuous line). The values for both flame-sprayed and plasma-sprayed copper lie well below the line. This may be interpreted as due to the fact that materials prepared by these techniques contain gross imperfections, and also that the individual particles are not joined by metallurgically sound bonds as in conventionally sintered powder compacts. Traces of oxide formed during preparation will also reduce the conductivity. On heating in vacuum the particles weld together progressively, leading to an increase in conductivity and an apparent hysteresis on temperature-cycling. At high temperature there is a further improvement as the oxide decomposes. The flame-sprayed copper reached the Grootenhuis line after heating to 800° C, but values for plasma-sprayed copper were still low even after sintering at 1000° C. Previous data by Osberg *et al* [13] for flame-

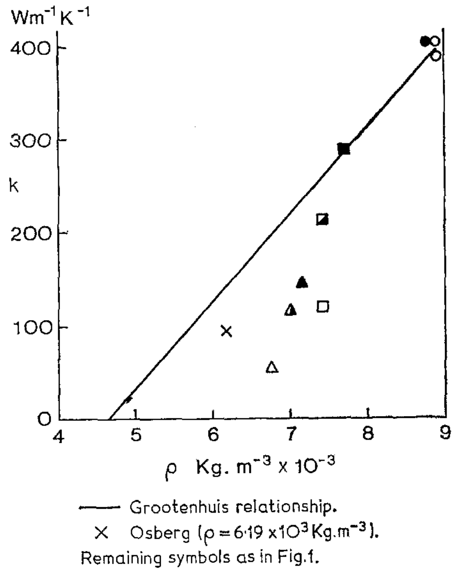

Figure 2 Porous copper: variation of thermal conductivity at 40° C with density.

sprayed copper (fig. 2) and Smirnov *et al* [14] for plasma-sprayed copper (fig. 1) are in general agreement with the picture presented by the present work. The general conclusion is that the Grootenhuis relationship, while applicable to normally sintered powder compacts, is not suitable for unsintered, sprayed copper although sintering does permanently increase the thermal conductivity to values significantly nearer the Grootenhuis line. The relationship given by Mitoff appears to be even less appropriate for this type of material.

Acknowledgement

The authors wish to thank Mr W. Lilley for arranging the supply and manufacture of the copper discs. The flame-sprayed material was obtained from the Bristol Metal Spraying and Welding Co Ltd.

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Received 29 March
and accepted 16 April 1971

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Short Notices

Solid State Surface Science: Volume I

Mino Green (editor)

Pp 420 (Marcel Dekker, New York, 1970) $18.50

This first volume of a new series contains articles on the nature and statistical thermodynamics of chemisorbed hydrogen on the surface anomaly of electrical transport in crystals, the structure of chemical complexes at semiconductor surfaces (the editor's special interest), a detailed survey on the methods of measuring the work function of surfaces followed by a critical survey of values for various materials, and an essay on properties (transport properties in particular) of epitaxial lead chalcogenide films compared with the same substances in bulk form. As is proper to the theme, the book pays equal attention to physical and chemical aspects of surfaces, and it should be of particular interest to readers in the semiconductor industry. R.W.C.