

Thermal conductivity of porous copper manufactured by the lost carbonate sintering process

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This article describes an experimental investigation on the thermal conductivity of open-celled porous copper manufactured by the Lost Carbonate Sintering process. The thermal conductivity was either measured directly using Corsan's method or calculated from electrical conductivity values using the Wiedemann–Franz law. The relationship between thermal conductivity and relative density followed the power

law, with the exponents being 2.05 for the former and 2.96 for the latter method. The thermal conductivity measured by Corsan's method was higher than that calculated from electrical conductivity, mainly because the sintering defects in the cell walls made contributions to thermal conduction but not to electrical conduction. The pore size had no significant effect on the thermal conductivity.

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1 Introduction Porous metals have received a growing interest throughout a number of different industries. They possess unique combinations of structural and functional properties, such as impact energy absorption capacity, air and water permeability in open-cell foams, unusual acoustic properties and good electrical shielding properties [1].

Open-celled cellular metals make attractive compact heat exchangers for applications where high efficiency in heat dissipation is demanded, e.g. heat sinks for high-power electronic devices operating at power densities in excess of 10^7 W/m² [2]. Copper conducts heat extremely well in its solid state and therefore the thermal properties of porous copper are of particular interest, especially when implemented as heat exchangers, heat sinks for power electronics, air-cooled condenser towers and regenerators [3]. The relatively low quantity of metal within a porous copper sample means that the thermal conductivity will be relatively low, when compared to the parent metal [1]. When used for a practical application, a trade-off between the density and effective thermal conductivity ensues.

Ogushi et al. measured and analysed the effective thermal conductivity of lotus-type porous copper [4]. They found that the material exhibited anisotropic properties for

the effective thermal conductivity when measured perpendicular and parallel to the pores. Babcsán et al. investigated the thermal and electrical conductivity measurements on closed-cell aluminium foams [5]. They discovered that the relationship between thermal conductivity and density exhibits almost linear behaviour.

The transport of heat across a porous metal with either open or closed cells is dominated by conduction along the solid cell walls and to a lesser extent by thermal radiation amongst the cell walls. With copper being an extremely good conductor of heat, it is expected that the conduction of heat through the cell walls will dominate the total heat transfer through the porous samples. The thermal conductivity of a porous copper sample is therefore mainly dependant on the relative density or porosity of the specimen, but is also dependant on the integrity and morphology of the cell walls or the morphology of the cells. The porosity and cell morphology are in turn dependant on the manufacturing technology and the process conditions adopted in fabricating the sample. In solid route manufacturing, impurities within the cell walls and rough surfaces will also affect the thermal conduction.

This paper measures the thermal conductivity of porous copper manufactured by the Lost Carbonate Sintering

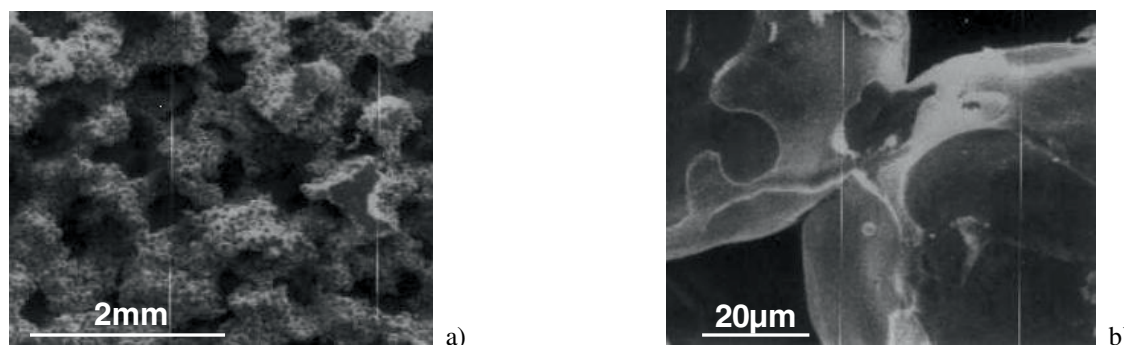


Figure 1 SEM photographs of a porous copper sample showing (a) spherically shaped pores and the irregular cell walls, and (b) bonding between two sintered copper particles.

(LCS) process and studies the effect of porosity and pore size.

2 Experimental A set of ten porous copper samples were manufactured using the LCS method, developed by Zhao et al. for manufacturing open-celled porous metals [6]. A commercially pure copper powder, consisting of spherical granules with diameters less than $75\ \mu\text{m}$ was mixed with a potassium carbonate (K_2CO_3) powder at a pre-specified volume ratio. The K_2CO_3 particles were spherical in shape and had diameters ranging between $425\ \mu\text{m}$ and $1500\ \mu\text{m}$. The K_2CO_3 powder was sieved and categorised into three particle sizes: $425\text{--}710\ \mu\text{m}$, $710\text{--}1000\ \mu\text{m}$ and $1000\text{--}1500\ \mu\text{m}$. The mixture was then compacted into a preform under a pressure of $250\ \text{MPa}$ within a steel tube, using a hydraulic press. The steel tube had an inside diameter of $21\ \text{mm}$. The preform was sintered in a furnace at a temperature of $850\ ^\circ\text{C}$ for four hours. The preform was then allowed to cool back to room temperature and the K_2CO_3 was dissolved in running water for three hours, leaving behind the porous copper network, whose pores are direct negatives of the K_2CO_3 particles. The pores within the sample are spherical and of a pre-specified size, determined by the K_2CO_3 powder used. The

pores are interlinked by small tunnels and have rough, irregular walls as a result of the sintered copper granules. Figure 1 shows the pore morphology and bonding between two sintered copper particles in one of the porous copper specimens.

A number of different test methods are available for measuring the thermal conductivity of different materials [7]. The thermal conductivity tests on the porous copper samples were carried out at atmospheric pressure using a method developed by Corsan [8]. Figure 2 shows a schematic diagram of the test apparatus. The porous copper specimen is cylindrical in shape and has a length $110\ \text{mm}$ and diameter $19\ \text{mm}$. A solid copper comparator of length $150\ \text{mm}$ and diameter $19\ \text{mm}$ was clamped down onto the test specimen using an aluminium clamping jig. Thermally conductive grease was applied to the end of the test specimen and the end of the comparator, so that the heat was conducted effectively through the interface. The clamp held the solid copper comparator and the porous copper sample together firmly and ensured a good contact at the interface.

Holes with a diameter of $2\ \text{mm}$ were drilled at specific, measured locations along the length of the comparator and the porous copper test specimen. Each hole had a K-type

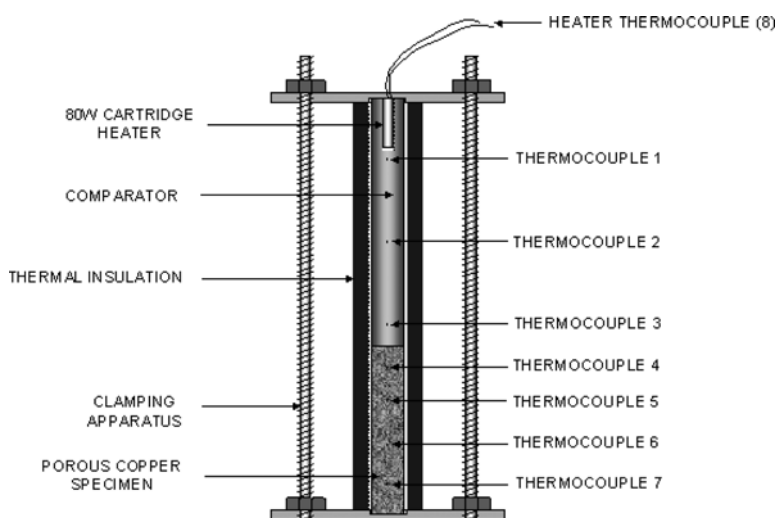


Figure 2 Schematic diagram of the test apparatus showing the clamping jig, test specimen and comparator set-up.

thermocouple located in it. The end of each thermocouple had a heat-shrunk plastic shroud around it to warrant a tight fit in the drilled hole and to ensure that the temperature reading was from the precise axial centre of the specimen. All the thermocouples were linked up directly to a data acquisition unit, with a resolution of 0.01 °C. The solid copper comparator had a 6 mm bore at the top end for an 80 W cartridge heater to be located. The heater was controlled using a variac so that a steady-state temperature could be achieved accurately at thermocouple 1, in the comparator. The test specimen and comparator were insulated circumferentially, using a combination of calcium-magnesium-silicate wool and polyethylene to minimise radial heat losses. Thermal insulation was also added between the comparator and the clamping jig to prevent heat conduction and subsequent dissipation through the aluminium apparatus. The lower plate of the clamping apparatus acts as a heat-sink for the test specimen, to ensure a steady temperature gradient. Figure 3 shows typical temperature plots of the 8 thermocouples as a function of time.

Once the temperature within the samples reached its steady-state (after approximately one hour, depending on the relative density of the sample), the temperature reading was taken at each of the thermocouple locations by the data acquisition unit. The steady-state temperatures at thermocouple 1 varied slightly among the samples, but all were in the range of 100 ± 6 °C.

The thermal conductivity of the porous copper sample was determined from the temperature gradients in the test specimen and comparator.

The heat flow rate of a one-dimensional steady state problem in any one conductor can be expressed as:

$$Q = \kappa A \left(\frac{\delta T}{\delta x} \right), \quad (1)$$

where Q is the heat flow rate, κ is the thermal conductivity, A is the cross-sectional area of the conductor and $\delta T/\delta x$ is the temperature gradient. Assuming that the porous copper specimen and the comparator were perfectly insulated circumferentially, the heat flow rate is a constant through-

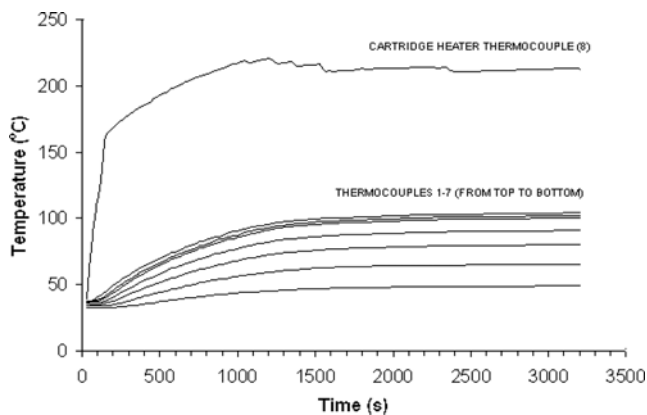


Figure 3 Typical temperature plots of the cartridge heater and thermocouples 1–7 for one of the samples.

out the porous specimen and the solid comparator. As the cross sectional area, A , is also the same in both the comparator and the porous specimen, the thermal conductivity of the porous copper, κ_2 , is given by:

$$\kappa_2 = \kappa_1 \frac{\left(\frac{\delta T}{\delta x} \right)_1}{\left(\frac{\delta T}{\delta x} \right)_2}, \quad (2)$$

where κ_1 is the thermal conductivity of the solid copper comparator, given by the manufacturer as 390 W m⁻¹ K⁻¹, $(\delta T/\delta x)_1$ is the temperature gradient in the solid copper comparator and $(\delta T/\delta x)_2$ is the temperature gradient in the porous copper test specimen. The temperature gradients in the comparator and the porous copper can be obtained from the temperature plots along the lengths of the comparator and the porous copper sample.

In order to verify the results obtained using the Corsan method for measuring thermal conductivity, the electrical conductivity of five test specimens was measured using a Sigmatest 2.068 conductivity meter. The instrument uses eddy currents to establish the resistance to the flow of current in the material and hence the conductivity. Since free electrons are responsible for both electrical and thermal conduction in pure metals, theoretical treatments suggest that the two conductivities should be related according to the Wiedemann–Franz law [9]. Assuming that the dominant mechanism for both electrical and thermal conduction in the porous copper specimen is conduction by free electrons, then the thermal conductivity of the specimen can be estimated from its electrical conductivity by the Wiedemann–Franz law as:

$$k = LT\sigma, \quad (3)$$

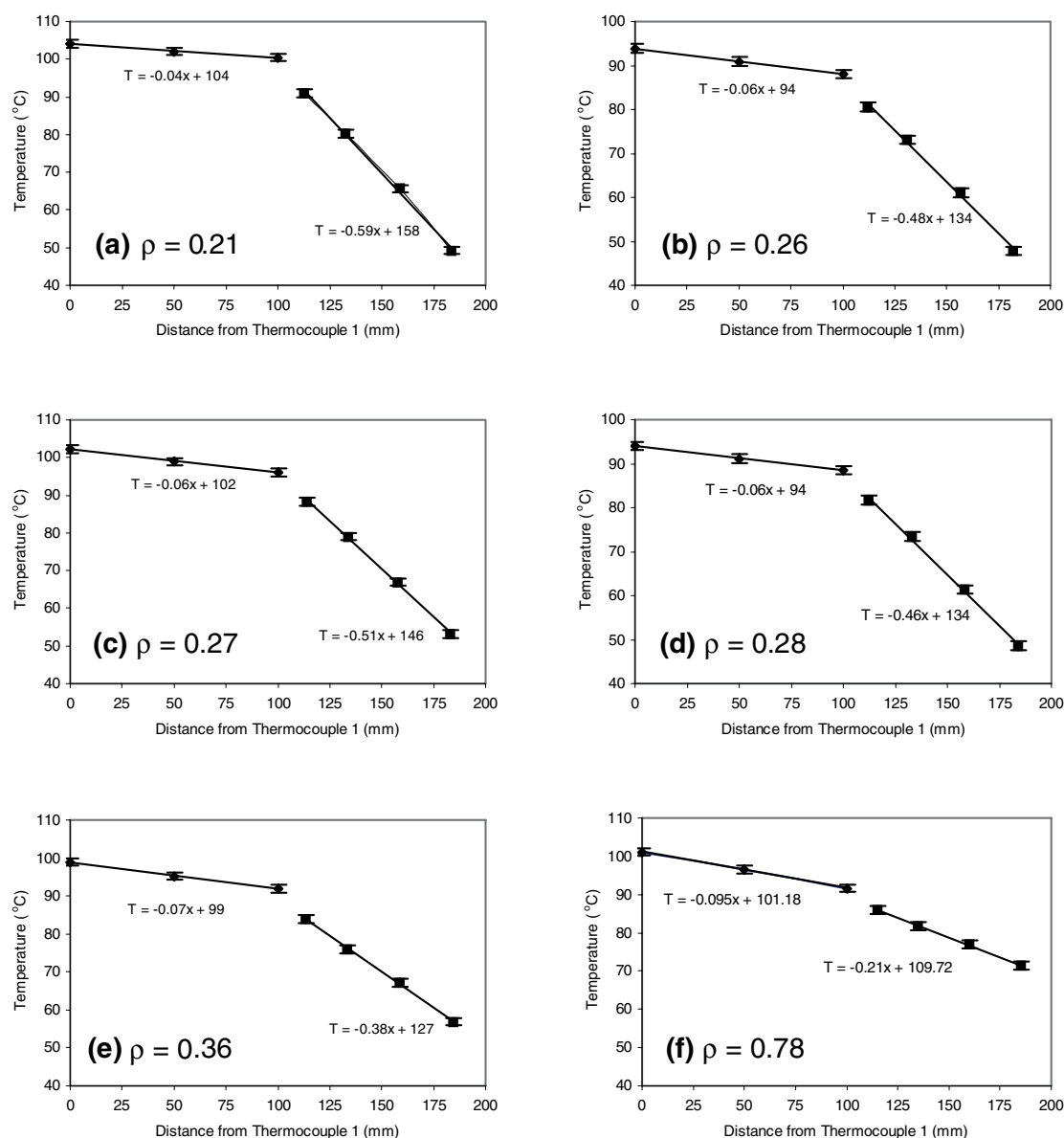
where k is the thermal conductivity, L is a constant with a theoretical value of $2.44 \times 10^{-8} \Omega \text{ W}/(\text{K})^2$, T is the absolute temperature, and σ is the electrical conductivity. It should be noted that L should be independent of temperature and equal for all metals provided that heat energy is transported entirely by free electrons. All measurements were taken at a room temperature of $23 \pm 0.5 \text{ °C}$.

3 Results and discussion The thermal conductivity of ten different specimens was measured and compared. Each sample has different properties, in terms of the relative density and pore size. The relative density is the ratio of the density of porous copper with the density of pure copper. It was measured using Archimedes method and is accurate to within ±0.005. The variation in density along the length of the sample is less than 6% based on quantitative metallographic measurements. The properties of the ten porous copper test samples are summarised in Table 1. Sample 10 was manufactured by sintering a bulk of copper powder with no space holder, that was compacted and sintered under the same process parameters as the other nine samples.

Table 1 Structural characteristics and thermal conductivity of porous copper samples.

| sample number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|--|----------|-----------|----------|---------|----------|---------|---------|---------|---------|------|
| relative density | 0.21 | 0.26 | 0.27 | 0.28 | 0.36 | 0.15 | 0.2 | 0.25 | 0.3 | 0.78 |
| porosity (%) | 79 | 74 | 73 | 72 | 64 | 85 | 80 | 75 | 70 | 22 |
| pore size (μm) | 710–1000 | 1000–1500 | 710–1000 | 425–710 | 710–1000 | 425–710 | 425–710 | 425–710 | 425–710 | – |
| thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$) | | | | | | | | | | |
| Corsan's method | 24.8 | 46.9 | 46.3 | 45.9 | 68.7 | – | – | – | – | 178 |
| Sigmatest method | – | – | – | – | – | 6.2 | 15.6 | 28.1 | 42.5 | 172 |

Figure 4 shows the temperature gradients in samples 1–5 and 10, and their corresponding comparators at steady-state temperatures in the range of $100 \pm 6^\circ\text{C}$ at thermocouple 1. The first three data points (up to 100 mm from thermocouple 1) represent the temperature readings of the three thermocouples in the comparator. The remaining four data points represent the thermocouple temperature readings in the porous copper specimen. The change

**Figure 4** Temperature gradients in the solid copper comparators and the porous copper samples 1 (a), 2 (b), 3 (c), 4 (d), 5 (e) and 10 (f).

in temperature gradient is clearly visible between thermocouples 3 and 4, where the interface between the comparator and the test sample is.

The plots in Fig. 4 show linear temperature gradients in both the solid copper parts and the porous copper parts, with the interface clearly visible in each case. This demonstrates negligible radial heat losses at steady-state temperatures within the range of 100 ± 6 °C. The temperature gradients in samples 1–5 and 10 and their corresponding comparators are: $-0.59, -0.04$; $-0.48, -0.06$; $-0.51, -0.06$; $-0.46, -0.06$; $-0.38, -0.07$; and $-0.21, -0.095$ K m^{-1} ; respectively. Using Eq. (2), the corresponding values for the thermal conductivity for samples 1–5 and 10 were calculated to be 24.8, 46.9, 46.3, 45.9, 68.7 and 178.0 $\text{W m}^{-1} \text{K}^{-1}$, respectively. Samples 2–4 all have relative densities between 0.26 and 0.28 and different pore sizes of 1000–1500 μm , 710–1000 μm and 425–710 μm respectively. The deviation in relative density between the samples is due to slight discrepancies during the manufacturing process. The results show that for a given relative density, the pore size only has a very slight effect on the thermal conductivity, with measured values varying between 45.9 $\text{W m}^{-1} \text{K}^{-1}$ and 46.9 $\text{W m}^{-1} \text{K}^{-1}$ for samples 2–4. The thermal conductivity of a porous copper sample is mainly determined by its relative density, or porosity.

The electrical conductivities of samples 6–9 and 10 were measured to be 1.0, 2.5, 4.5, 6.9 and 28.2 MS m^{-1} respectively. The corresponding values of the thermal conductivities calculated from Eq. (3) were 6.2, 15.6, 28.1 42.5 and 172.0 $\text{W m}^{-1} \text{K}^{-1}$, respectively. The room-temperature electrical conductivity of pure copper is 60 MS m^{-1} [9]. The experimental data of thermal conductivities for all ten samples are plotted as a function of relative density in Fig. 5. This shows that the thermal conductivity is dominated by the relative density or porosity of the porous copper sample.

Empirical correlation and modelling have shown that the relationship between the thermal conductivity and the relative density of the porous metal can be expressed by

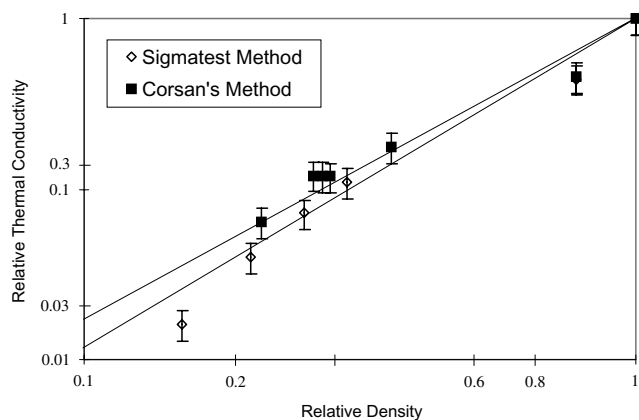


Figure 5 Double-log plot showing the variation of thermal conductivity with relative density, measured by Corsan's method and the Sigmatest method.

power law [10–13]:

$$\frac{\kappa}{\kappa_0} = \left(\frac{\rho}{\rho_0} \right)^n, \quad (4)$$

where κ is the thermal conductivity of the porous metal, κ_0 is the thermal conductivity of the bulk material in the cell wall, ρ is the density of the porous metal, ρ_0 is the density of the bulk metal and n is the exponent for thermal conductivity. The theoretical value predicted by the percolation theory for the exponent for thermal conductivity is $n = 2.0$ [14]. The relative thermal conductivity vs. relative density curves fitted to Eq. (4) are also shown in Fig. 5. The power law with exponents of 2.05 and 2.96 describes the experimental data well for Corsan's method and the Sigmatest method, respectively. It clearly shows that for any relative density, the thermal conductivity value obtained by the Sigmatest method was lower than that obtained by Corsan's method.

There are four mechanisms contributing to the heat transfer and thus the thermal conductivity of the porous copper samples. These mechanisms are thermal conduction through the cell walls, thermal conduction through the gas within the pores and interconnecting channels, convective effects within the pores and radiation through the cell walls. By far the most dominant of these mechanisms is solid conduction through the cell walls, however the other three will firstly be considered.

If the relative density of the porous metal is increased, the connectivity between pores will decrease, resulting in a reduction in radiative heat transfer between pores through interconnecting channels. Radiation through the cell walls is not possible in a case of optically non-transparent metals. Radiation within the cells can be ignored, when the thermal conduction of the cell wall material is greater than 20 $\text{W m}^{-1} \text{K}^{-1}$ [3].

Gaseous conduction in an open cell porous metal depends greatly on the relative density of the porous metal. The gas in the pores is air and the value of thermal conductivity for air at atmospheric pressure is 0.025 $\text{W m}^{-1} \text{K}^{-1}$ [3], which is well below the thermal conductivity of solid copper. The heat transfer via gaseous conduction is not significant, for samples with relative density above 0.2.

Convection within the cells is important only when the Grashof number (the ratio between force driving convection and opposing viscous force) is greater than about 1000 [3]. In order for convection to take place, there needs to be sufficient space within a pore where a temperature difference can be present so that the convection current can be present. For this reason, the effect of heat transfer by convection will be greater in sample 3, due to the larger pore size. However, convection in porous metals with a pore size less than about 10 μm is negligible [15].

The overwhelming majority of the heat transfer through each of the porous copper samples is via solid conduction through the cell walls. Increasing relative density of the porous copper sample increases the volume of

the cell walls, which in turn increases the thermal conductivity. This can clearly be seen in Fig. 5.

If the cell walls were defect free solid copper and electron movement were the only mechanism for both electrical and thermal conductivity, then electrical conductivity and thermal conductivity of the porous copper samples would be expected to conform to the same power law in Eq. (4) with an exponent n close to 2. Figure 5 shows that both the variations of electrical conductivity and thermal conductivity with relative density follow a power law, confirming that electron movement is the main mechanism for electrical and thermal conduction in the cell walls. However, the exponent of the thermal conductivity curve determined by Corsan's method is lower than that of the curve determined by the Sigmatest method. At any relative density, the thermal conductivity measured by Corsan's method is higher than that calculated from electrical conductivity by Eq. (3). To explain this phenomenon, the integrity of the cell walls and the other mechanisms contributing to thermal conduction must also be considered.

In fact, the cell walls are not perfect solid copper but contain numerous defects formed during the manufacturing process. There exist low conductive metal oxides, impurities, cracks and various other defects within the cell walls, characteristic of sintered components. These defects can largely impede the flow of electrons and thus significantly reduce the electrical conductivity. The measured electrical conductivity is expected to be lower than that predicted for perfect cell walls and the fitted power law has a higher exponent of 2.96.

The thermal conductivity in solid walls has another contributing mechanism. In addition to electron conduction, lattice vibration waves, or phonons, can also transport heat. While most of the sintering defects in the cell walls are electrical insulators, they can still contribute to thermal conduction. In other words, while radiative heat transfer, gaseous conduction and convection are all negligible, the conduction by phonons is not. For these reasons, the thermal conductivity values obtained using Corsan's method were significantly higher than those converted from the electrical conductivity values obtained using the Sigmatest method.

4 Conclusions The thermal conductivity of six open-celled porous copper specimens manufactured using the Lost Carbonate Sintering method was measured and calculated experimentally, using a novel method developed by Corsan. Heat transfer through the porous copper was dominated by conduction in the solid phase, with heat transfer via convection, radiation and gaseous conduction being negligible. The thermal conductivity increases with relative density and fits the power law, with a value for the

exponent for thermal conductivity of 2.05. Electrical conductivity of five samples, manufactured using the same process, was also measured. The electrical conductivity values were converted to thermal conductivity values using the Wiedemann–Franz law. The as-obtained thermal conductivity also increases with relative density and fits the power law, with a higher exponent of 2.96. The disparity in the thermal conductivity values between these two methods is mainly because the sintering defects in the cell walls, such as oxides and impurities make contributions to thermal conduction but not to electrical conduction. The pore size of the porous metal does not have any significant effect on the thermal conductivity.

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References

- [1] G. J. Davies and S. Zhen, *J. Mater. Sci.* **18**, 1899 (1983).
- [2] A. F. Bastawros and A. G. Evans, *Proc. Symp. on the Application of Heat Transfer in Microelectronics Packaging (IMECE)*, Dallas, TX, 1997.
- [3] H. Degischer and B. Kriszt (eds.), *Handbook of Cellular Metals (Wiley-VCH, Berlin, 2002)*, pp. 222–224.
- [4] T. Ogushi, H. Chiba, H. Nakajima, and T. Ikeda, *J. Appl. Phys.* **19**, 5843–5847 (2004).
- [5] N. Babcsán, I. Mészáros, and N. Hegman, *Mater.-wiss. Werkst.tech.* **34**, 391–394 (2003).
- [6] Y. Y. Zhao, T. Fung, L. P. Zhang, and F. L. Zhang, *Scr. Mater.* **52**, 295–298 (2005).
- [7] British Standard: Methods for determining thermal insulating properties with definitions of thermal insulating terms, BS 874:1973.
- [8] J. M. Corsan, *Physica E, Sci. Instrum.* **17**, 800–807 (1984).
- [9] W. D. Callister, *Materials Science and Engineering – An Introduction*, 5th ed. (John Wiley and Sons, Inc., USA, 2000), pp. 662–665.
- [10] J. Kovacik et al., in *Proc. Int. Conf. Effect of Non-Standard External Factors on Physical Properties of Solids (Military Academy Liptovsky Mikulas, 1996)*, p. 57.
- [11] J. Kovacik and F. Simancik, *Scr. Mater.* **39**, 239 (1998).
- [12] J. Kovacik, *Acta Mater.* **46**, 5413 (1998).
- [13] J. Kovacik and F. Simancik, in: *Metal Foams and Porous Metal Structures*, edited by J. Banhart, M. F. Ashby, and N. A. Fleck (MIT Verlag, Bremen, 1999), p. 303.
- [14] D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, 2nd ed. (Taylor and Francis, London, 1992).
- [15] G. V. Jackson and A. G. Leach, *J. Phys. D, Appl. Phys.* **26**, 740–745 (1993).