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THERMAL CONDUCTIVITY OF CEMENTED CARBIDES

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Hard-metals are powder metallurgical composites made from carbides or carbonitrides of refractories with minor amounts of a ductile binder phase. Their thermal conductivity is very important as concerns their behaviour under thermomechanical loading in use. For practicable and quick measurement, a stationary method and a non-stationary one were introduced. The experimental results show that the thermal conductivity of hard-metals varies over the wide range between 10 and 100 $\mathrm{Wdeg^{-1}m^{-1}}$, mainly reflecting the nature of the hard phase and its defect structure. The dependences on the position of the refractory in the Periodic Table and on the stoichiometry are discussed. For hard-metals based on titanium carbide, the thermal conductivity is proportional to the electrical one, i.e. the Wiedemann-Franz law holds with a modified Lorentz factor.

Hard-metals are powder metallurgical composites made from carbides or carbonitrides of refractories with minor amounts of a ductile binder phase. These materials exhibit a unique combination of hardness and toughness, bridging the gap between metals and ceramics. Accordingly, they are outstandingly suitable for tools and wear-resistant parts. In such applications, thermal conductivity is an essential parameter. It governs the stationary temperature level in the tool during turning, and hence wear by diffusional processes or plastic deformation. Furthermore, under non-stationary loading, as in milling or laser irradiation, it determines temperature gradients, thermal stresses and, finally, thermal shock damage. Thus, the thermal conductivity λ appears explicitly in the thermal shock resistance $R' = \sigma_c\lambda/E\alpha$ (σ_c = strength, E = elastic modulus, α = thermal expansion coefficient), describing the cracking behaviour under severe thermal shock.

It is therefore urgently needed to characterize not only the mechanical behaviour, but also the thermal conduction of such materials. The methods should be employable as routine measurements for continuous control in material development and fabrication. This means that they should be performable quickly and with conventional sample shapes. The thermal conductivity lies between 10 and 100 $\mathrm{Wdeg^{-1}m^{-1}}$ for the materials under consideration. An accuracy of better than ±20% is sufficient for control and estimation of the service behaviour. A stationary and a nonstationary method were chosen. In order to avoid long balancing times, they work near room temperature. The potentials of the practicable versions developed for

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this purpose are demonstrated for hardmetals as the most important class of tool materials. Conventional ones based on tungsten carbide, as well as newly-developed materials based on titanium carbide and carbonitride, were investigated.

Experimental methods

The first of the chosen methods involves a stationary relative measurement of the thermal conductivity λ. It is based on the stationary equilibrium between energy input and heat transfer to the surroundings. One end-face of the rod-like sample (standard dimensions 5 mm X 5 mm X 35 mm) is electrically heated up to a constant temperature T_b, whereas the other surfaces are in free contact with the surrounding air (Fig. 1a). The heat flux q within the rod is given by $q = -\lambda \mathrm{d}T/\mathrm{d}x$ (transverse heat transport is neglected due to the slenderness of the sample). The heat flux q_s towards the surroundings is determined by the heat transfer coefficient h (of the order of 50 $\mathrm{W deg^{-1} m^{-2}}$ in air): $q_s(x) = h(T(x)-T_s)$, where T_s denotes the temperature of the air far away from the heated rod. The temperature distribution along the specimen in the stationary case follows from the balance of these energy fluxes: $T(x)-$ $-T_s = (T(0)-T_s)\,(\cos h(g\sqrt{b}\,x) + \sqrt{b}/g \sin h\,(g\sqrt{b}\,x))$, with $g = \sqrt{S/A}$ (S and A are the circumferential length and cross-sectional area of the sample, respectively), and $b = h/\lambda$. From the temperatures at two places x_1 and x_2, measured with thermocouples, the unknown quantity $b = h/\lambda$ can be determined by a graphical method. Assuming that the heat transfer does not depend on the material the thermal conductivity λ of the investigated material can be calculated from b by comparison with the values λ_o and b_o for a known gauge sample. Here, nickel was used with $\lambda_o = 86\ \mathrm{W deg^{-1} m^{-1}}$, determined by the non-stationary absolute method discussed below. The experimental uncertainty was estimated as ±15%. Special attention must be paid to the thermal contact of the thermocouples with the sample, and to the controlled surrounding conditions by careful shielding.

The other method chosen here involves non-stationary absolute measurement of thermal diffusivity $a = \lambda / c\rho$ (c = specific heat, ρ = density) by a simple version of flash methods. In principle, the same arrangement as above has been used (Fig. 1b), but contact with the bath of temperature T_b is restricted to short times by dipping the sample into hot water or molten tin. The temperature rise at the free end-face opposite the heated one is measured with a thermocouple. For contact times Δt much smaller than

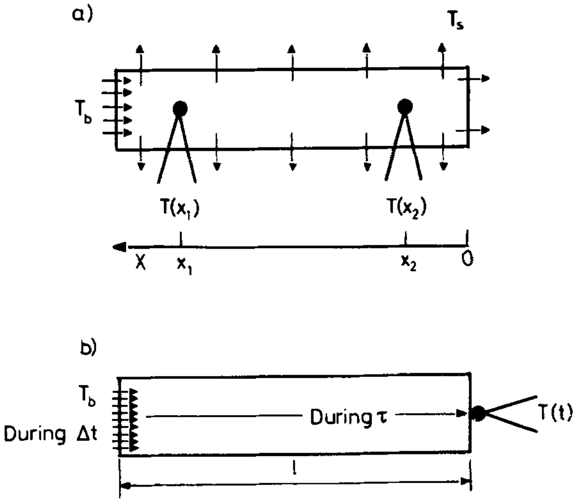

Fig. 1 Scheme of the applied methods
a) stationary relative measurement of thermal conductivity λ;
b) non-stationary absolute measurement of thermal diffusivity *a*

the characteristic time τ necessary for heat diffusion $\tau \approx l^2/a$ (l = sample length), half of the total temperature increase is reached after the time $t_{0.5} = 0.14\ l^2/a$. For our samples, these times are of the order of 10 s, long enough for problem-free measurement and short enough for heat transfer to the surroundings to be neglected. Thus, thermal diffusivity can be directly determined from the plot $T(t)$ of the end-face temperature. The experimental uncertainty $\Delta a/a$ is about ±10%. For comparison of the two methods and mutual transformation of λ and $a = \lambda/c\rho$, specific heat c and density ρ were determined by conventional mixing and buoyancy methods, respectively.

In parallel with the thermal transport properties, the electrical conductivity σ was measured. For this, a four-point method was used. The experimental error of the latter is smaller than ±1%.

Results and discussion

As a rule, the λ values obtained with the two methods for the same sample are within the bounds of experimental uncertainty. Some systematic deviation cannot be excluded, with a tendency to higher (smaller) values from the non-stationary method for specimens with higher (smaller) thermal conductivity, corresponding to materials with dominating tungsten (titanium) carbide. The non-stationary method used works at some higher mean temperature, where the thermal conductivity decreases for tungsten and increases for titanium carbide, respectively.

A large variety of hard-metals with different types of hard phases (tungsten carbide, mixed titanium-tungsten and titanium-molybdenum carbides and carbonitrides) were investigated. The experimental results show that the thermal conductivity varies over a large range, between about 10 and 100 $\mathrm{Wdeg^{-1}m^{-1}}$. The binder phase should be of minor importance for the transport properties in these composite materials: By partial dissolution of the carbide phase, the metallic binder becomes high-alloyed and hence the mean free path for electrons and phonons is strongly reduced. For instance, the electrical resistivity of cobalt increases from 6 μOhm cm in the pure state to about 50 μOhm cm in the WC-Co composite [1], thereby achieving a value of the same order as the electrical resistivities of the carbides (WC: 20 μOhm cm, $\mathrm{Ti(C_{1-x}N_x)_z}$ 50 to 150 μOhm cm, depending on x and z). Therefore, as a first approximation, the influence of the binder state on the thermal conductivity can be neglected because of its small content of only 5 to 15 vol.% in the investigated materials. The variations in the thermal conductivity reflect the nature and the perfectness of the carbides or carbonitrides. Due to the mixed bonding, with metallic, ionic and covalent contributions, both electrons and phonons are effective as carriers in energy transport. Their contributions depend on the density of conducting electrons and the defect structure. The former is determined by the positions of the metallic and the non-metallic components in the Periodic Table and is thus given by the type of the hard phase. A decisive factor is the content of the VIa elements tungsten and molybdenum in the hard phase (Fig. 2). For an atomic fraction of these (with respect to the total refractories) below 2/3, the thermal conductivity lies in a broad, nearly constant range of 10 to 30 $\mathrm{Wdeg^{-1}m^{-1}}$. At higher W and Mo contents, λ rises steeply up to about 90 $\mathrm{Wdeg^{-1}m^{-1}}$ for WC-Co. The outstanding thermal conductivities of WC-Co cemented carbides compared with those of TiC(N)-based hard-metals (corresponding to those of the carbides: $\lambda(\mathrm{WC}) = 120\ \mathrm{Wdeg^{-1}m^{-1}}$, and $\lambda(\mathrm{TiC_z}) = 10\ldots30\ \mathrm{Wdeg^{-1}m^{-1}}$ is mainly caused by the higher number of conducting electrons of VIa elements as compared with IVa elements. For the pure metals: $\lambda(\mathrm{W}) = 168\ \mathrm{Wdeg^{-1}m^{-1}}$, and $\lambda(\mathrm{Ti}) = 21\ \mathrm{Wdeg^{-1}m^{-1}}$. This difference is amplified by the strong stoichiometry of the hexagonal tungsten monocarbide, whereas the cubic titanium carbides or carbonitrides usually show a marked deficiency of the non-metallic components. The vacancies in the non-metallic sublattice act as scatter centers for both

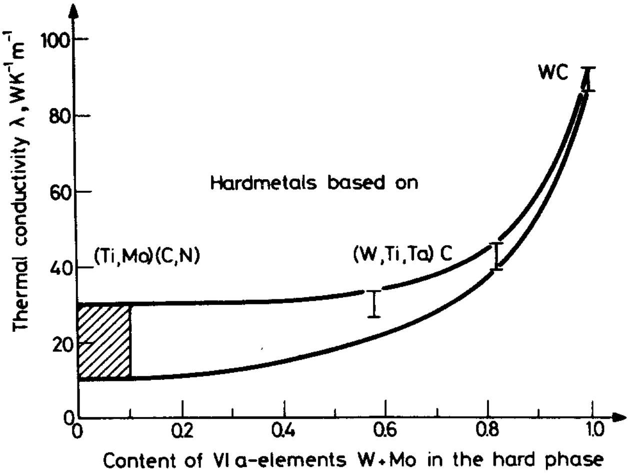

Fig. 2 Dependence of thermal conductivities of various hard-metals on their content of tungsten and molybdenum (atomic fraction with respect to the total refractories in the hard phase)

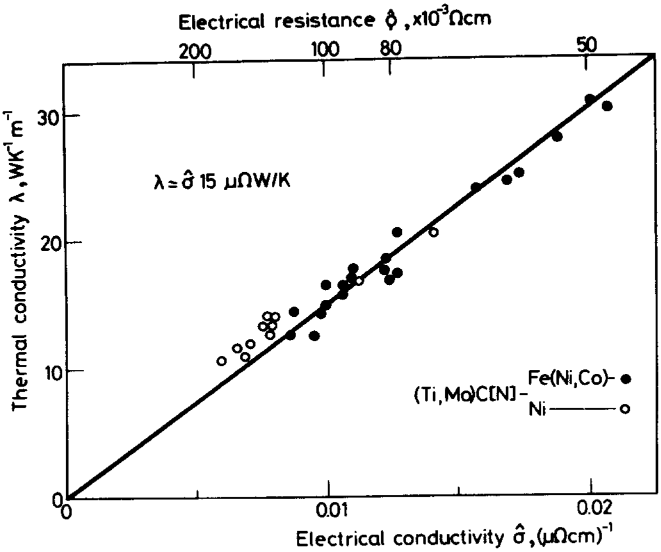

Fig. 3 Relation between thermal conductivity λ and electrical conductivity σ̂ for various hard-metals based on titanium carbide

phonons and electrons [2]. Their density can be changed widely by technological modifications. Because of the related scattering of phonons and electrons, the thermal conductivities of hard-metals based on titanium carbide are proportional to the electrical conductivities. The Wiedemann-Franz law, $\lambda = \hat{\sigma}\, L_o T$ ($L_o = 2.2\ 10^{-8}$ Ohm Wdeg^{-2}, holds with a modified Lorentz factor L: $\lambda = \hat{\sigma}\ 15 \cdot 10^{-3}$Ohm Wdeg^{-1}(Fig. 3). Comparison with the electronic part of the thermal conductivity, approximated by $\lambda_{el} = \hat{\sigma}\, L_o T = \hat{\sigma}\ 6.6 \cdot 10^{-3}$ Ohm Wdeg^{-1}, shows that at near room temperature the electrons and phonons contribute with equal weights. Therefore, for the class of titanium carbide hard-metals the measurement of thermal conductivity can be replaced by measurement of the more easily available electrical conductivity. If hard phases with other compositions (especially with carbonitrides or with higher VIa element contents) are included, this simple relation based on the related change of electron and phonon scattering breaks down, because changing of the conducting electrons does not influence the energy transport by phonons in the same way.

References

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Zusammenfassung – Hartmetalle sind pulvermetallurgisch hergestellte Verbundwerkstoffe aus Carbiden oder Carbonitriden mit geringen Mengen eines duktilen Bindemittels. Ihre Wärmeleitfähigkeit ist von grosser Bedeutung für das Verhalten unter thermomechanischer Belastung bei ihrem Einsatz. Zur einfachen und schnellen Messung werden eine stationäre und eine instationäre Methode aufgebaut. Experimentell wurde festgestellt, dass die Wärmeleitfähigkeit der Hartmetalle im bereich 10–100 W $K^{-1}m^{-1}$ variieren kann, in Abhängigkeit von der Natur der harten Phase und ihrer Defektstruktur. Der Einfluss der Stellung der Metallkomponente im Periodischen System und der Stöchiometrie wird diskutiert. Die Wärmeleitfähigkeit von Hartmetallen auf Titancarbidbasis ist proportional ihrer elektrischen Leitfähigkeit, das heisst das Wiedemann-Franz'sche Gesetz gilt mit einem modifizierten Lorentz-Faktor.

РЕЗЮМЕ — Тугоплавкие металлы являются порошкообразными металлургическими композитами, получаемые из огнеупорных карбидов или карбонитридов с незначительными добавками пластичных присадок. Термическая проводимость является важной характеристикой их поведения при термомеханической нагрузке. Для ее практического и быстрого измерения установлены стационарный и один не стационарный метод. Экспериментальные результаты показали, что термопроводимость тугоплавких металлов изменяется в широкой области значений от 10 до 100 В/К$^{-1}$ м$^{-1}$, отражая тип твердой фазы и дефекты ее структуры. Обсуждена зависимость между положением тугоплавких металлов в периодической таблице элементов и стехиометрией твердых металлов. Для тугоплавких металлов на основе карбида титана термопроводность пропорциональна электрической, т.е. подчиняется закону Видемана-Франца с измененным числом Лоренца.