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Mechanical and Thermophysical Properties of Hardmetals at Room and Elevated Temperatures

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Abstract

Hardmetals or cemented carbides are a widely-used material in cutting applications. To reach maximum efficiency in the cutting process the choice of the proper hardmetal grade is crucial. Often the selection is solely based on mechanical properties such as hardness and fracture toughness while in some cutting applications the selection should also be based on the thermal conductivity too. Thus, for cutting applications both mechanical and thermophysical properties are equally important. In this study different WC-Co hardmetals with the same nominal hardness at room temperature were fabricated by varying both WC grain sizes from nanoscaled to coarse and metallic (Co) binder contents. Hardness and thermal conductivity were determined in the range from room temperature up to 900 °C. Results show significant differences in thermal diffusivity and high temperature hardness of the materials with the same room temperature hardness. The influence of the microstructure on these properties will be discussed.

1. Introduction

Hardmetals or cemented carbides offer excellent mechanical properties, i.e. high hardness and sufficient toughness. This makes them suitable for a wide range of applications such as cutting, drilling or wear protection. The hardness of hardmetals mainly depends on the composition and microstructure, i.e. WC grain size and metallic binder content. With decreasing WC grain size and Co content the hardness increases [1]. Especially with the use of very coarse or very small WC grains a huge hardness area can be covered. Thus, hardness values from below 1000 HV to up to 2200 HV can be achieved with a Co content of 10 wt-% [2].

Several different models have been developed to predict the hardness by correlating hardness with microstructural parameters. Many models are based on the empirical model by Lee and Gurland from 1978 [3]. In this model the rule of mixture is applied to calculate the hardmetal hardness $H_{WC\text{-}Co}$. The hardness of the components WC and Co is described by a Hall-Petch type relationship, respectively. As can be seen in Eq. 1 $H_{WC\text{-}Co}$ is calculated from WC grain size d_{WC}, mean free path length of Co d_{Co}, volume fraction of WC V_{WC}, the WC contiguity C and empirically derived constants.

$$H_{WC-Co} = 1382 + 23.1\, {d_{WC}}^{-1/2} \cdot V_{WC} \cdot C + \left(304 + 12.7\, {d_{Co}}^{-1/2}\right) \cdot (1 - V_{WC} \cdot C) \qquad \text{Eq. 1}$$

It is known that this model overestimates the hardness of hardmetals with WC grain sizes in the submicron to nano range. Numerous other models have been developed as well [4–6] such as the semi-empirical model by Makhele-Lekala et al. [7], whose formula is shown in Eq 2.

$$H_{WC-Co} = 4100 \cdot \left(k' \cdot \left(\frac{d_{Co}}{2\sqrt{d_{WC}}} \right)^{\frac{1}{2}} + 1 \right)^{-1} - 130\; with\; k' = 22.3\; mm^{-1/4} \qquad \text{Eq. 2}$$

In general the hardness of hardmetals decreases with increasing temperature. As could be shown by different authors [8, 9], fine grained hardmetals retain higher hardness than coarse grained hardmetals up to a certain temperature. Above this temperature (500 °C according to [8], ≈ 930 °C according to [9]) coarse grained hardmetals retain higher hardness.

Hardmetals are composites, which means that both the ceramic hard phase WC as well as the metallic binder phase Co contribute to the hardmetal's overall thermal conductivity. In principle it is possible to apply the rule of mixture to calculate the composites thermal conductivity κ [10]. The main influences on

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thermal conductivity of hardmetals are the volume fraction of metallic binder as well as the WC grain size. In general the thermal conductivity increases with decreasing Co content because the κ of the ceramic phase is higher compared to the metallic binder phase. For pure WC thermal conductivities between 100 and 200 W/mK were reported while for Co around 70 to 100 W/mK were measured [10–12]. Typical WC-Co hardmetals have a thermal conductivity in the range of 100 W/mK [13]. Defects in the microstructure such as porosity, vacancies or grain boundaries act as scatter centers for both electrons and phonons which both conduct heat in hardmetals. Thus, with increasing defect density thermal conductivity diminishes. This means that with increasing WC grain size (i.e. decreasing number of interfaces per volume unit) the thermal conductivity increases. So far no clear correlation between carbide contiguity or microstructural inhomogeneities on the thermal conductivity could be demonstrated [14]. In principle the amount of dissolved W and C in the metallic binder should change the κ of the metallic binder as well. A decrease of κ with decreasing carbon content is reported in literature [10, 11], but it is not clear whether the change in κ originates in the difference of alloy composition or in the effect of carbon content on grain growth and thereby on final grain size.

In this study hardmetals with similar hardness at room temperature are produced by varying both WC grain size and metallic binder content. The different resulting microstructures (nano to fine with 5 wt% to 20 wt% Co) and the thermal conductivities are studied. Both hardness and thermophysical properties are investigated at elevated temperatures of up to 1000 °C as well.

2. Experimental

Hardmetals with varying WC grain size were produced using a conventional powder technological route. Four different mixtures were prepared using three differently sized WC powders, varying amounts of Co powder and different amounts of the grain growth inhibitors Cr_3C_2 and VC. The powder particle sizes and suppliers are listed in Table 1. The particle sizes were measured with a Fisher Sub Sieve Sizer (FSSS) and also calculated from the measured BET specific surface area [15].

Table 1: Powder properties

Powder designation	Supplier	Specific surface BET / m²/g	Particle size (d_{BET}) / nm	Particle size (d_{FSSS}) / µm
WC DN 4.0	H.C. Starck Tungsten	4.0	97	0.30
WC DS80	H.C. Starck Tungsten	1.3	291	0.80
WC DS250	H.C. Starck Tungsten	0.4	953	2.9
Co Half Micron	Umicore	3.3	205	0.7
Cr_3C_2 160	H.C. Starck	2.0	450	1.8
VC HV160	H.C. Starck	3.0	350	1.2

An overview of the produced hardmetal mixtures is shown in Table 2. The mixtures were ball-milled in heptane for 12 h to 24 h hours, dried and sieve granulated. Samples were uniaxially pressed, debinded in hydrogen atmosphere and afterwards sintered at 1350 °C in a SinterHIP furnace for 45 min with 60 bar gas pressure (Ar).

Table 2: Powder mixtures

Mixture designation	Co / wt%	Cr_3C_2 / wt%	VC / wt%	WC powder	Milling time / h
A	5	-	-	WC DS250	12
B	10	0.7	-	WC DS80	12
C	15	0.8	0.3	WC DN4.0	24
D	20	1.8	1.2	WC DN4.0	24

Samples were characterized in terms of their magnetic properties, (coercivity H_c according to ISO 3326 and magnetic saturation polarization mS with adjustment of Cr content as described in [16]). Polished samples were used to study the microstructure using a field emission scanning electron microscope (Ultra 55, Carl Zeiss NTS GmbH). Micrographs were also used to perform linear analysis and calculate stereological parameters such as the arithmetic average WC grain size d_{WC} (ISO 4499-2, linear intercept method). The Vickers hardness of the samples was determined according to ISO 3878 with an indentation load of 10 kp in the temperature range between room temperature and 900 °C. Thermal diffusivity α was measured with the Laser Flash Analysis method according to DIN EN 821 in the temperature range between room temperature and 1000 °C. The thermal conductivity κ was estimated by multiplying the thermal diffusivity α with a calculated specific heat capacity and the room temperature density. The density as measured by the Archimedes method accordingto ISO 3369. The specific heat capacity was calculated with the software FactSage (version 7.0, with Scientific Group Thermodata Europe (SGTE) 2014 database.

3. Results and Discussion

Room temperature properties

Four different hardmetal grades with similar hardness at room temperature were produced by varying both WC grain size and Co content. The magnetic properties of these hardmetals are shown in Table 3. The increasing values of coercivity already indicate the intended decreasing WC grain size from grade A to D.

Table 3: Magnetic properties of hardmetals with same hardness and varying WC grain size and binder content

Grade	Co / wt%	Magnetic saturation / μTm^3kg^{-1}	Magnetic saturation / % theoretical	Coercivity Hc / kA/m
A	5	8	80	13
B	10	16	84	18
C	15	24	84	21
D	20	33	88	28

Micrographs of the microstructure of all four grades are shown in Fig. 1. All produced hardmetals have a homogeneous microstructure and no free carbon or eta phase was detected.

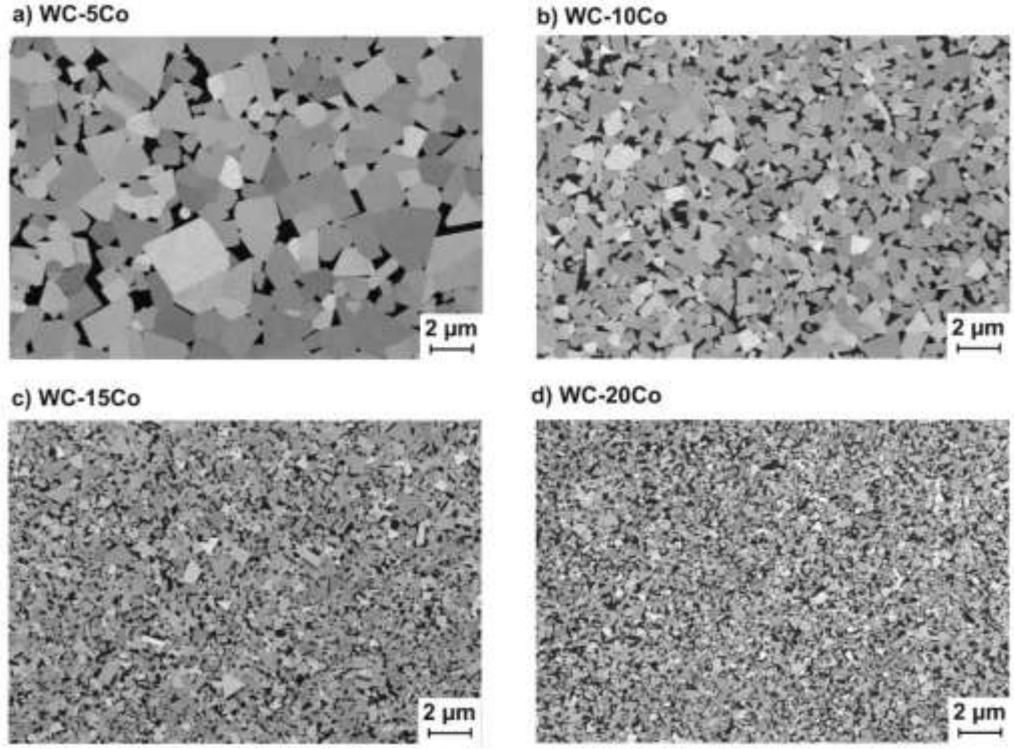

Fig. 1: Micrographs of WC-Co samples with varying WC grain size and binder content

The linear intercept method was used to describe the microstructure quantitatively. The results are listed in Table 4. The expected and measured binder content agree well (the expected binder content was estimated to be the addition of the nominal Co and Cr_3C_2 content). Besides the arithmetic mean WC grain size d_{WC} the characteristic points of the cumulative distribution of WC grain size d_{10}, d_{50} and d_{90} were calculated. The WC grain size d_{WC} clearly decreases from the coarsest grade A to the finest grade D from 1 µm to 0.1 µm. The mean free binder path d_{Co} and the WC contiguity C decrease accordingly as well.

Table 4: Results of linear analysis (linear intercept method)

Grade	Expected binder content	Measured binder content	WC grain size				Co mean free path	Contiguity
	vol%	vol%	d_{WC} / µm	d_{10} / µm	d_{50} / µm	d_{90} / µm	d_{Co} / µm	C
A	9	9 ± 1	1.02 ± 0.02	0.32	0.88	1.87	0.30 ± 0.02	0.67
B	18	17 ± 2	0.44 ± 0.01	0.13	0.40	0.81	0.19 ± 0.01	0.52
C	25	24 ± 2	0.29 ± 0.01	0.08	0.24	0.53	0.15 ± 0.01	0.39
D	33	32 ± 3	0.14 ± 0.01	0.04	0.12	0.25	0.10 ± 0.01	0.34

The hardness as well as thermal diffusivity α and thermal conductivity κ at room temperature (RT) were measured and are listed in Table 5. All grades have a similar measured hardness of 1540 HV10 ± 60 HV10 and a varying thermal diffusivity and conductivity. As expected the thermal conductivity decreases from grade A to D from 142 W/mK to 35 W/mK. This is due to both the increasing Co content and the decreasing WC grain size.

Table 5: Hardness and thermophysical properties of hardmetals at room temperature

Grade	Hardness/	Calculated hardness		α at RT /	κ at RT /
	HV10	Lee & Gurland[3] HV10	Makhele-Lekala[7] HV10	mm^2/s	W/mK
A	1560 ± 5	1692	1487	50 ± 3	142
B	1600 ± 5	1762	1516	27 ± 2	81
C	1490 ± 5	1749	1530	16 ± 1	49
D	1500 ± 10	1965	1546	11 ± 1	35

The parameters d_{WC}, d_{Co} and C determined by linear analysis were used to calculate hardness values, (also given in Table 5) using two different empirical models. While the hardness values calculated with the classic formula by Lee and Gurland [3] (Eq. 1) are too high compared to measured hardness values, especially in the case of very small WC grain sizes, the Makhele-Lekala et al. model [7] (Eq. 2) yielded good results for all four hardmetal grades. For the thermal conductivity exists also an empirical formula [10] which didn't yield plausible results in comparison to the measured values.

Properties at elevated temperatures

A typical application for hardmetals is cutting, where working temperatures of several hundred degrees Celsius occur. For this reason the change in hardness and thermophysical properties in the temperature range between room temperature (RT) and 900 °C was investigated. The hardness as a function of temperature and the relative decrease in hardness (in relation to RT) are shown in Fig. 2.

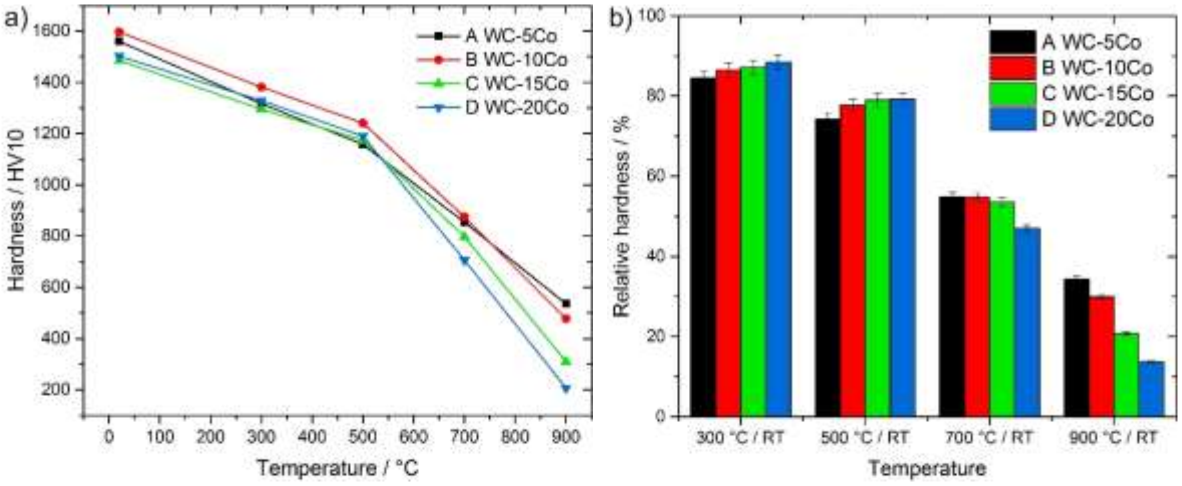

Fig. 2: (a) Hardness of WC-Co samples as a function of temperature (b) Relative decrease in hardness from 20 °C to 900 °C

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A difference between the lower temperature range and higher temperature range is noticeable: in the range from RT to approx. 500 °C the relative decrease in hardness of all four hardmetal grades is nearly constant, but there is a slight tendency that the fine grained, high binder content hardmetal grades C and D retain hardness better than grades A and B. At temperature above approx. 500 °C the coarse grained hardmetal grades with low binder content A and B show a lower relative decrease in hardness. This agrees well with findings of other authors as described in the introduction.

The thermal diffusivity and thermal conductivity as a function of temperature are shown in Fig. 3.

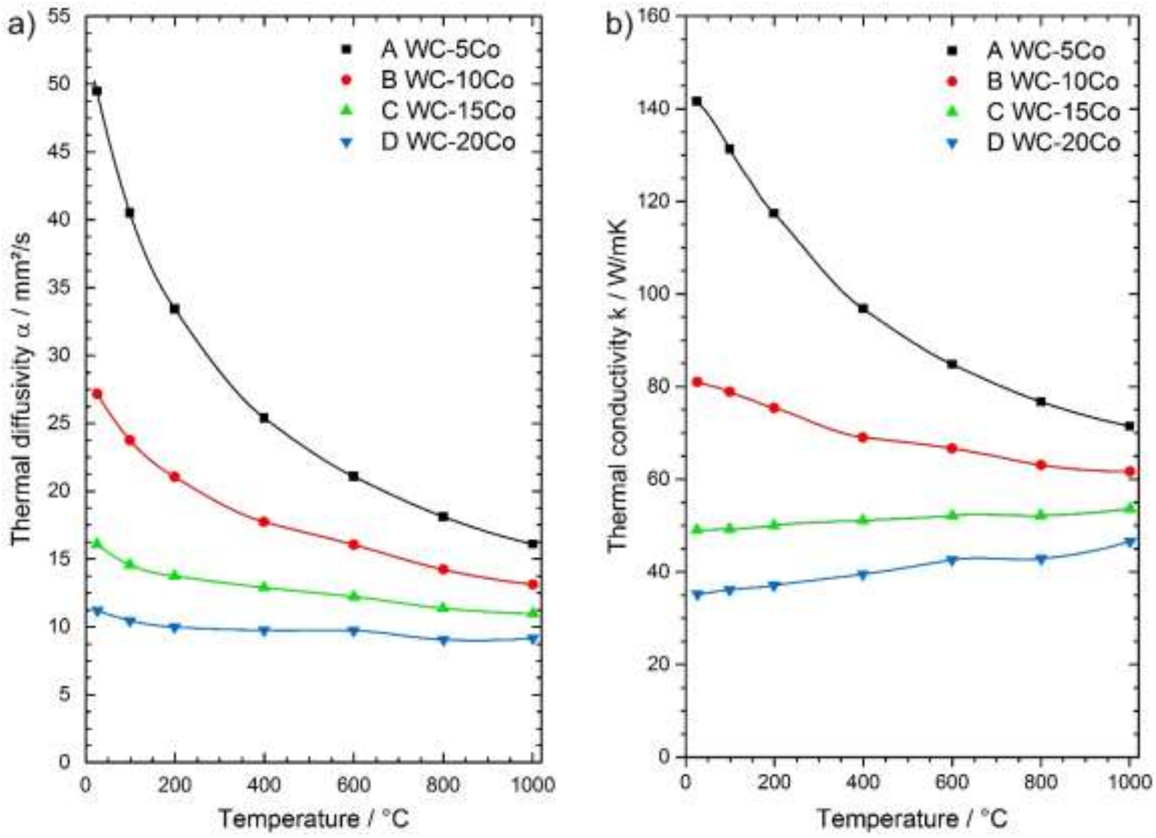

Fig. 3: (a) Thermal diffusivity and (b) thermal conductivity of WC-Co samples as a function of temperature

At room temperature the thermal diffusivity as well as the thermal conductivity of grade A is approx. 4 to 5 times larger compared to grade D. This difference decreases with increasing temperature. At 1000 °C the thermal diffusivity and conductivity of grade A is only around 2 times larger than grade D.

4. Conclusions

By varying both WC grain size and the metallic binder content it was possible to produce WC-Co hardmetals which have the same nominal hardness at room temperature but different thermal conductivities. The hardness and thermophysical properties were investigated in the range from room temperature to up to 900 °C. Thermal conductivity decreased with increasing metallic binder content and decreasing WC grain size. The difference in thermal conductivity at room temperature diminished with increasing temperature. It was found that fine grained hardmetals with high binder content tend to retain hardness at temperatures between 20 °C and approx. 500 °C slightly better than coarse grained hardmetals with low binder content. Above 500 °C this trend is inverted and the coarse grained hardmetals with low binder content show a distinctly lower decrease in hardness.

Future work will include a similar investigation at a higher and/or lower room temperature hardness level. Furthermore, addition of cubic carbides such as TiC, which influence thermal conductivity in hardmetals significantly, will be studied. Another interesting aspect is the investigation of the influence of added grain growth inhibitors and the overall influence of the binder saturation.
This work is part of an ongoing effort to develop a model to predict hardness and thermal conductivity at room temperature and elevated temperatures by correlating these properties with the microstructure.

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