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Application of Empirical Hardness Models on Hardmetals with Alternative Binders

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Abstract

Cemented carbides or hardmetals are materials with excellent hardness and toughness. The most widely used composition consists of tungsten carbide (WC) and the metallic binder cobalt (Co). Frequent price fluctuations as well as changes in the risk assessment of Co as a hazardous material (EU REACH) have led to renewed efforts in the search for a suitable substitute and its evaluation. Promising candidates include iron based binders such as iron-nickel-cobalt (FeNiCo). The mechanical properties of cemented carbides are closely correlated with the composition and microstructure. Several empirical models exist for the hardness of WC-Co composites and can be used for tailoring the material properties to the requirements of different applications. In this work hardmetals with various different metal binders have been produced and characterized in respect of their microstructure and hardness. The measured hardness values were compared with the values calculated with different empirical models.

1. Introduction

Cemented carbides or hardmetals are composite materials which offer excellent mechanical properties, i.e. high hardness and sufficient fracture toughness. These materials are used in a wide range of applications such as drilling, cutting or wear protection. The most widely used composition consists of tungsten carbide (WC) and the metallic binder cobalt (Co). Both recurrent Co price hikes as well as changes in the risk assessment of Co as a hazardous material (EU REACH) have led to renewed efforts in the search for a suitable substitute and its evaluation [1, 2]. Nickel (Ni) and iron (Fe) are chemically similar to Co and have thus been extensively studied. It could be shown that hardmetals with binder alloys based on Fe-Co-Ni have good mechanical properties [3].

The hardness of hardmetals is mainly influenced by the composition and microstructure, i.e. the metallic binder content and the WC grain size. With decreasing Co content and WC grain size the hardness of the composite increases [4]. A number of different models have been developed to predict the hardness by correlating it with microstructural parameters. The empirical model by Lee and Gurland from 1978 [5] is often referenced and considered a ‘classic model’. This model uses the rule of mixture to calculate the overall hardness $H_{WC\text{-}Co}$. Hall-Petch type expressions are used to describe the hardness of the components WC and Co. As shown in Eq. 1 the composite hardness $H_{WC\text{-}Co}$ is calculated from WC grain size d_{WC}, mean free path length of the Co binder λ, volume fraction of WC V_{WC}, WC contiguity C and empirically derived constants.

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

It has been shown that this model overestimates the hardness of very fine grained hardmetals with WC grain sizes in the submicron to nano range [6]. Several other models have been developed afterwards [7–10], such as the empirical model by Roebuck et al. [11], whose formula is shown in Eq 2.This model is basically based on the Lee and Gurland’s one because it also utilizes the Hall-Petch relationship.

$$H_{WC-Co} = (888 - 9.9 \cdot wt\%Co) + \frac{229 + 532 \exp\left(-\frac{wt\%Co - 6}{6.7}\right)}{\sqrt{d_{WC}}} \qquad \text{Eq. 2}$$

The need for such hardness models for hardmetals with alternative binders has been recognized and Walbrühl et al. have recently presented a hardness model for Fe-Ni-Co based cemented carbides [12]. This model requires computational calculations to obtain the binder hardness. This study instead aims to modify existing empirical hardness-microstructure formulas to make a quick and simple estimation of the hardness of alternative binder based hardmetals.

2. Experimental

Hardmetals with alternative binders Ni, Fe and FeNiCo (40 wt%Fe, 40 wt% Ni, 20 wt% Co) were produced using a conventional powder technological route. WC-Co hardmetals have also been produced as a reference point. Three powder mixtures were prepared for each binder type: (1) WC with d_{FSSS} of 1.4 µm with 19 vol% binder ("WC(A)-19x"), (2) WC with d_{FSSS} of 1.4 µm with 28 vol% binder ("WC(A)-28x") and (3) WC with d_{FSSS} of 2.9 µm with 19 vol% binder ("WC(B)-19x"). No grain growth inhibitors were added. The powder suppliers and the particle sizes 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 [13].

Table 1: Powder properties

Powder designation	**Supplier**	**Specific surface BET / m²/g**	**Particle size (d_{BET}) / nm**	**Particle size (d_{FSSS}) / µm**
WC DS120	H.C. Starck Tungsten	0.8	480	1.4
WC DS250	H.C. Starck Tungsten	0.4	953	2.9
Co Half Micron	Umicore	3.3	205	0.7
Ni	Eurotungstene	0.9	720	2.6
Fe	Cerametal	4.6	171	1.5
FeNiCo 40/40/20	H.C. Starck	-	-	1.2

The powder mixtures were ball-milled in n-heptane for 20 h, dried and sieve granulated. Samples were uniaxially pressed, debinded in hydrogen atmosphere and sintered at 1350 °C in a SinterHIP furnace for 45 min with 60 bar Ar gas pressure. Additionally pure binder metal samples were produced by melting the metal powders in alumina crucibles at temperatures between 1485 °C and 1510 °C.

The microstructure was studied using a field emission scanning electron microscope (Ultra 55, Carl Zeiss NTS GmbH). The arithmetic average WC grain size d_{WC} was determined using the linear intercept method according to ISO 4499-2. The Vickers hardness of the hardmetal samples was determined according to ISO 3878 with an indentation load of 10 kp. The binder samples were measured with a reduced indentation load of 1 kp.

3. Results and Discussion

Hardmetal samples with four different binder metals (Co, Ni, Fe, FeNiCo) were produced. As described in the experimental section three different samples were studied for each binder type: (1) sample with 19 vol% binder (equates 12 wt% Co, "WC(A)-19x") (2) sample with 29 vol% binder (equates 18 wt% Co, "WC(A)-28x") and (3) sample with 19 vol% binder and coarser WC starting powder ("WC(B)-19x"). The measured hardness and the results of the linear analysis (arithmetic average WC grain size d_{WC}, mean free length of binder λ and contiguity C) are shown in Table 2.

First of all, a clear influence of the binder type on the d_{WC} can be seen when the sintered WC grain sized of the samples with 19 vol% binder and the smaller WC starting powder "WC(A)" are compared to each other: the WC-Fe sample has the smallest sintered WC grain size of 0.4 µm while the samples with FeNiCo and Co binder have slightly larger WC grain sizes of 0.5 µm and 0.6 µm, respectively. The WC-Ni sample has a significantly larger WC grain size of 1 µm. This WC grain growth retarding (Fe) or enhancing (Ni) effect of alternative binders has already been described in other studies [14, 15]. In conformity with the WC grain sizes, the WC-Fe sample has the highest measured hardness (1479 HV10) and the WC-Ni sample the lowest hardness (1094 HV10). However, the hardness of the WC-Co sample is higher (1330 HV10) compared to the WC-FeNiCo sample (1276 HV10) although the WC grain size of the former sample is slightly larger. This is due to the difference in binder hardness.

Table 2: Measured properties of sintered hardmetals

Designation	d_{WC} / µm	λ / µm	Contiguity	Hardness/ HV10
WC(A)-19Co	0.60	0.30	0.51	1330
WC(A)-28Co	0.66	0.40	0.42	1096
WC(B)-19Co	0.82	0.39	0.48	1275
WC(A)-19Ni	0.97	0.49	0.47	1094
WC(A)-28Ni	2.48	1.51	0.25	714
WC(B)-19Ni	1.12	0.50	0.50	1053
WC(A)-19Fe	0.39	0.17	0.50	1479
WC(A)-28Fe	0.43	0.24	0.40	1189
WC(B)-19Fe	0.44	0.18	0.50	1416
WC(A)-19FeNiCo	0.49	0.24	0.55	1276
WC(A)-28FeNiCo	0.56	0.43	0.52	1038
WC(B)-19FeNiCo	0.63	0.32	0.51	1175

The measured microstructure parameters were used to calculate the hardness using Lee and Gurland's and Roebuck et al.'s models. The calculated hardness values are compared to the measured values in Figure 1. Lee and Gurland's model overestimates the hardness in case of all hardmetal grades. On the other hand, Roebuck et al.'s model yields very accurate results for the WC-Co and also for WC-Fe samples with a difference of 1 % to 2 % to the measured value. However, the hardness of the samples with Ni and FeNiCo binder is overestimated by this model as well.

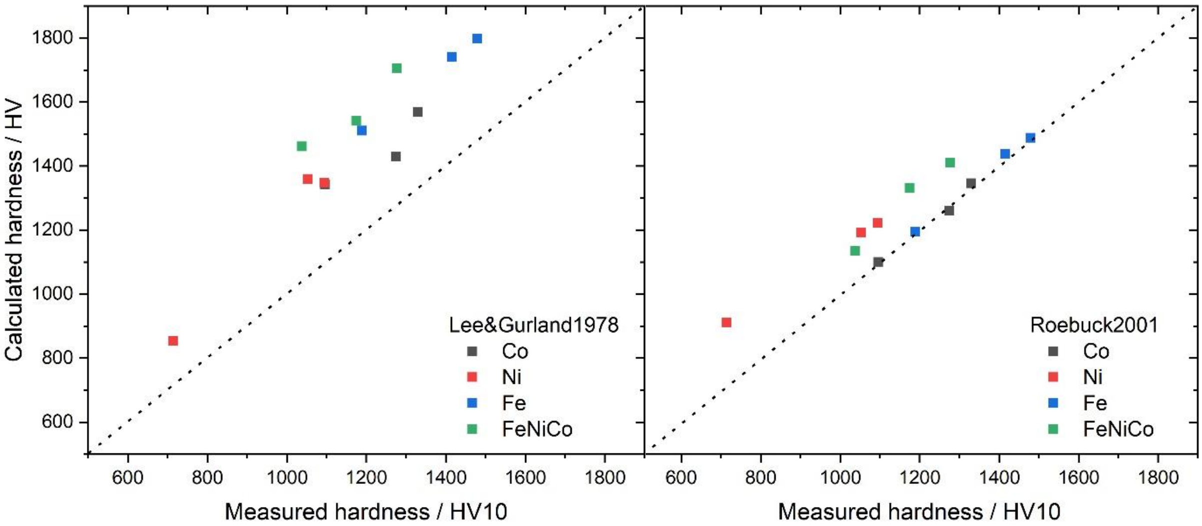

Figure 1: Calculated hardness compared to measured hardness, left: Lee and Gurland's model, right: Roebuck et al.'s model

The empirical models are based on WC hardmetals with Co binder and thus a correction for the different hardness of alternative binders has to be made. There are different approaches available to determine the binder hardness, e.g. the in-situ measurement of nano-hardness in binder areas of sintered hardmetals [16] or calculation by computational methods [12]. The chosen approach in this study is the measurement of the hardness using pure binder metal samples. The density and hardness of these Co, Ni, Fe and FeNiCo metal samples is listed in Table 3. The Co sample has the highest hardness of 133 HV1, followed by the FeNiCo sample with 110 HV1. The Fe and the Ni sample have considerably lower hardness values of 86 HV1 and 64 HV1, respectively.

Table 3: Measured properties of binder metal samples

Binder	**Density / g/cm³**	**Relative density / %**	**Hardness / HV1**	**Hardness relative to Co**
Co	8.47	95.3	133	1.00
Ni	8.90	99.9	64	0.48
Fe	7.86	99.8	86	0.65
FeNiCo	8.37	99.0	110	0.83

The authors are aware that this measured bulk hardness is different to the actual binder hardness, which is strongly influenced by the amount of C and W in solution as well as other aspects, i.e. residual thermal stress or binder crystal structure. Still the hardness of the different binder metals can be compared to each other in this way. The hardness ratio of alternative binder metals to the Co hardness value was calculated to the ratio values shown in Table 3. These values were used as a correction factor F_x in the adjusted WC-Co based empirical hardness models to see if the WC-Co hardness models can be modified for use with WC-x (x=alternative binder) hardmetals.

To do this, the binder hardness term in Lee and Gurland's model is multiplied with the correction factor F_x as shown in Eq 3. In case of Roebuck et al.'s model the correction factor F_x was inserted into the first term of the formula. Thus, as can be seen in Figure 2, the calculated hardness of compositions with low binder content is hardly influenced by the correction factor while the calculated hardness of compositions with high binder content is, as desired, considerably modified.

$$H_{WC-x} = 1382 + 23.1\, {d_{WC}}^{-1/2} \cdot V_{WC} \cdot C + \boldsymbol{F_x}\left(304 + 12.7\, \lambda^{-1/2}\right) \cdot \left(1 - V_{WC} \cdot C\right) \qquad \text{Eq. 3}$$

$$H_{WC-x} = \left(888 - \frac{\mathbf{1}}{\boldsymbol{F_x}} \cdot 9.9 \cdot wt\%x\right) + \frac{229 + 532\exp\left(-\frac{wt\%x - 6}{6.7}\right)}{\sqrt{d_{WC}}} \qquad \text{Eq. 4}$$

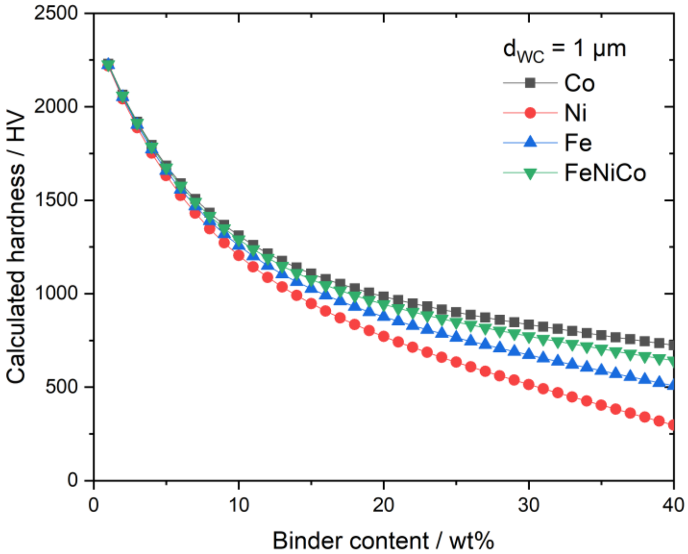

Figure 2: Calculated hardness for hardmetals with a WC grain size of 1 µm and different binders, using Roebuck et al.'s model with a correction factor

Hardness values were again calculated with the empirical models, but using the correction factor F_x (Eq. 3 and Eq. 4). A comparison of the calculated hardness to measured values of the studied samples is given in Figure 3.

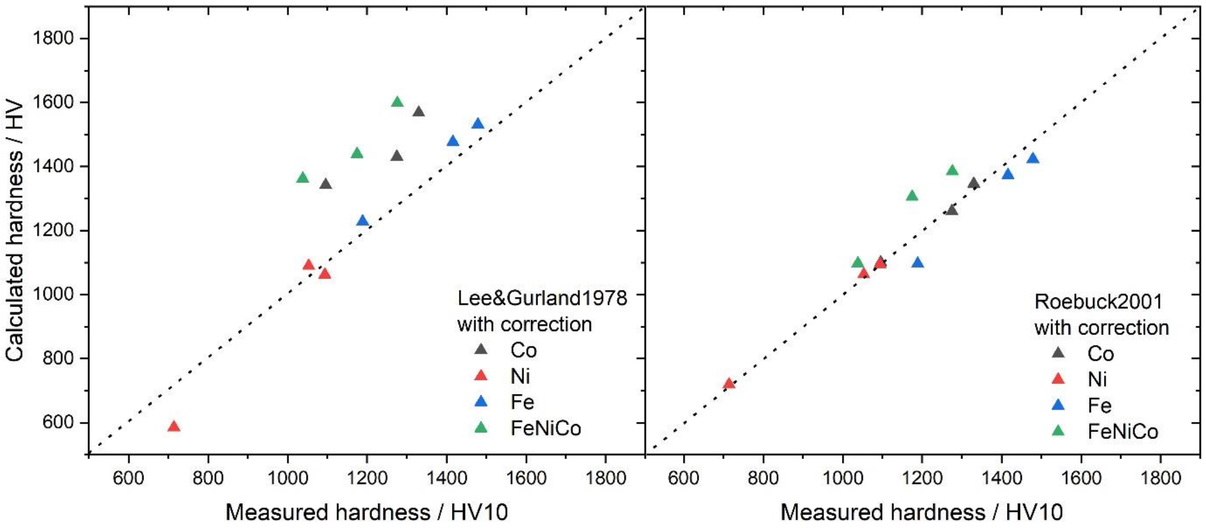

Figure 3: Calculated hardness with correction for alternative binders compared to measured hardness, left: Lee and Gurland model, right: Roebuck et al. model

Looking at Lee and Gurland’s model it can be seen that calculated values are closer to measured hardness values with the correction factor, but still some deviations persist. The calculated values of the WC-Fe samples are quite close to the measured values (3 % to 4 % difference compared to the 22 % to 27 % deviation without the correction). The calculated hardness of the WC-Ni samples with 19 vol% binder also agree well with the measured data. But the hardness of the WC-Ni sample with high binder content of 28 vol% is clearly underestimated, probably due to the strong grain growth and low contiguity of only 0.25. In case of the WC-FeNiCo samples the calculated values are closer to the measured values with the correction, but still a considerable deviation similar to the deviation of the WC-Co samples exists. Overall this model is of limited use for the studied hardmetals due to the small WC grain size. Still it shows the possibility of introducing a correction factor to account for different binder metals than Co.

The hardness values calculated with Roebuck et al.’s model fit the experimental data of the WC-Co and WC-Fe samples well, as was already shown in Figure 1. By introducing the correction factor the calculated hardness of the WC-Fe samples is now underestimated. This is due to the difference in the measured binder metal hardness between Co and Fe. The hardness of Fe is very dependent on the amount of carbon in solid solution. The Fe metal sample was not alloyed with carbon and thus the hardness is lower compared to the hardness of the Fe binder in the actual hardmetal sample. A Fe binder metal sample alloyed with W and C would therefore yield a more accurate correction factor.

In case of WC-Ni samples the calculated values with the correction agree very well with the measured hardness with a deviation of just 0 % to 1 %. But WC-FeNiCo samples still show a clear difference between calculated and measured hardness of 6 % to 11 %, even with the correction included. The correction factor that was derived from the measured binder metal sample (0.8) is apparently too high. But even by using a smaller correction factor of e.g. 0.6 the calculated hardness does not agree with measured values for all three WC-FeNiCo samples. This means that the empirical hardness model for WC-Co hardmetals can be applied to hardmetals with alternative binders by introducing a correction factor if the binder is an unalloyed metal such as Ni or Fe. In case of a metal alloys such as FeNiCo larger deviations persist even with the correction factor indicating that here, too, the alloying especially of Fe based binders with carbon and tungsten has to be considered.

4. Conclusions

Hardmetals with different alternative binders, i.e. Ni, Fe and FeNiCo, were studied and compared to conventional WC-Co hardmetals with regard to the relationship between microstructure and hardness. The hardness was measured and then compared to calculated hardness values which were obtained by using existing empirical hardness models for WC-Co hardmetals. While the Roebuck et al. model yields very accurate results for both WC-Co and WC-Fe samples, the calculated hardness of hardmetals with Ni and with FeNiCo binder is overestimated. By measuring the hardness of binder metal samples a correction factor was derived and used to express a WC-x (x=alternative binder) hardness model. In case for the WC-Ni hardmetals this modified model yields accurate results while in case of the binder alloy FeNiCo the model has to be further modified. However, in principle this modified hardness model for hardmetals with alternative metal binders can be used for a quick and uncomplicated estimation of the hardness using only the WC grain size and binder content without the need for computational methods or nano-indentation measurements. Further work includes the validation of the modified hardness model for a wider range of WC grain sizes and binder contents as well as the study of metal alloy binders and the influence of alloying elements.

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