ELSEVIER

International Journal of Refractory Metals & Hard Materials 19 (2001) 245–249

International Journal of
REFRACTORY METALS
& HARD MATERIALS

www.elsevier.com/locate/ijrmhm

Semi-empirical relationship between the hardness, grain size and mean free path of WC–Co

L. Makhele-Lekala [a,b], S. Luyckx [c,*], F.R.N. Nabarro [a,d]

[a] Materials Physics Institute, University of the Witwatersrand, Johannesburg, South Africa
[b] Technology Services International, Eskom, Centurion, South Africa
[c] School of Process and Materials Engineering, University of the Witwatersrand, Johannesburg, South Africa
[d] Division of Materials Science and Technology, CSIR, Pretoria, South Africa

Received 5 May 2001; accepted 21 May 2001

Abstract

The Vickers hardness of several well-characterized grades of WC–Co (23 in total) was measured. The mean grain size of these samples ranged from 0.6 to 5.0 μm and the cobalt content from 6 to 50 wt%. An empirical formula between hardness of WC–Co, grain size of WC and mean free path in Co was obtained. It was found that the empirical formula fitted our measured hardness well. However, when used against results of other researchers, it did not reproduce them satisfactorily at values higher than 1500 HV. A theoretical model, based on the assumption that plastic deformation of WC–Co begins at the WC–WC necks and that the mean length of the cross-section of the WC–Co necks is proportional to the square root of the mean WC grain size, was subsequently derived. The results obtained from this model were in good agreement with those of the empirical formula and like the empirical formula, did not reproduce high hardness values of other researchers. Thus, the model was modified by introducing semi-empirical terms which led to a satisfactory fitting of the data.

1. Introduction

The properties of tungsten carbide cobalt (WC–Co) have been extensively studied [1–5], due to its importance in industrial applications. WC–Co has a variety of applications, and the requirements of its properties may vary with application. The mechanical properties, such as hardness and fracture toughness, are dependent on its microstructural parameters. Experiments by Lee and Gurland [1] show that the hardness of WC–Co depends not only on the grain size of WC but also on the volume fraction of WC, the mean free path of the binder and the contiguity of WC particles. However, a general theory for the dependence of hardness of WC–Co composites on microstructural parameters has not yet been presented. It is in part the purpose of this investigation to develop a theoretical model for the relationship between WC–Co hardness, WC grain size and Co mean free path. Another reason for the present investigation is the derivation of an empirical formula relating hardness to WC grain size and mean free path of Co, without the explicit inclusion of WC contiguity.

2. Experimental details

WC–Co samples of cobalt content ranging from 6 to 50 wt% listed in Table 1 were prepared as described in [6]. For hardness tests, samples were mounted in a Bakelite mould and the exposed base surfaces of the samples were polished using diamond powder of particle size down to 0.25 μm on the Struers DP Mol Cloth. After polishing, they were cleaned by immersing them in alcohol and treated ultrasonically. Hardness tests were performed as per ISO 3878 [7] using a Leco V-100-A2 Vickers hardness testing machine. The recorded hardness values are the average measurements of two or more samples of the same grade measured at three different indentations per sample. A careful examination of the microstructure of WC–Co, in particular the WC grain size, was done by a Nikon Optiphot 55260 optical microscope and a scanning electron microscope (SEM), JEOL JSM-840. Prior to examination, polished surfaces

* Corresponding author.
E-mail address: sluyckx@chemeng.chmt.wits.ac.za (S. Luyckx).

0263-4368/01/$ - see front matter
PII: S0263-4368(01)00022-1

Table 1
Properties of all grades tested

Grade	Cobalt (wt%)	Average hardness (kg/mm^2)	Mean free path, λ (μm)	Grain size, d (μm)
UF10	10	1798	0.20	0.60
UF12	12	1684	0.25	0.62
UF14	14	1540	0.26	0.59
UF16	16	1424	0.28	0.65
UF30	30	1000	0.67	0.66
UF40	40	801	0.96	0.61
UF50	50	657	1.22	0.56
F10	10	1544	0.30	1.07
F20	20	1232	0.60	0.96
F30	30	960	1.05	0.84
F40	40	765	1.41	0.86
T6	6	1518	0.50	2.66
T8	8	1407	0.66	2.65
T18	18	1019	1.69	3.47
T50	50	498	7.37	3.27
C6	6	1289	1.12	5.32
C8	8	1187	1.18	5.21
C10	10	1138	1.40	4.77
C18	18	878	2.72	5.65
C20	20	829	2.91	5.08
C30	30	666	5.04	4.86
C40	40	508	6.26	4.13
C50	50	447	10.75	4.71

of the WC–Co specimens were chemically etched with a Murakami solution which attacks the carbide particles while the cobalt is almost unaffected. For the SEM examination, samples were coated with carbon. The WC grain size and the mean free path in Co were measured by linear analysis as described in [6]. The results are shown in Table 1.

3. Empirical model

As mentioned in the introduction, the hardness of WC–Co depends on its microstructural parameters such as the WC grain size, d, and the mean free path in cobalt, λ. We investigate the form of the dependence of the hardness of WC–Co, $H_{\mathrm{WC-Co}}$, on d and λ by deriving an empirical formula using our measured data. Since nonlinear functions are more general than linear ones and from the experimental results, according to which $H_{\mathrm{WC-Co}}$ increases nonlinearly with decreasing d and λ we propose a nonlinear function for the hardness $H_{\mathrm{WC-Co}}$ of the form

$$H_{\mathrm{WC-Co}}(\alpha; d, \lambda) = \alpha_1 + \alpha_2 d^{\alpha_3} \lambda^{\alpha_4}, \tag{1}$$

where $\alpha_1,\ \alpha_2,\ \alpha_3$ and α_4 are the fitting parameters to be determined. We do this via the nonlinear least-squares method. We define a chi-square function χ^2 and determine the best fit parameters by minimization of

$$\chi^2 = \sum_{i=1}^{N} [H_i - H_{\mathrm{WC-Co}}(\alpha; d, \lambda)]^2 \tag{2}$$

with respect to the parameters. In (2) the H_i's are the experimentally obtained values of hardness, d is the grain size of the WC and λ is the mean free path in Co. N is the number of data points to which the model is to be fitted. The starting point in solving Eq. (2) is to obtain the so-called normal equations – found by taking the partial derivatives of χ^2 with respect to each parameter α_i. The resulting normal equations, unlike those in the case of linear models, are functions of the parameters. As such the equations cannot be solved directly. In other words the minimization must proceed iteratively (i.e. given a trial vector α_0 for the parameters, one develops a procedure that improves α_0 to obtain the next best α). There are several numerical methods that can be used to obtain the solution to the normal equations. In our case we used the variant of the *Levenberg–Marquardt method* which has been found to be applicable over a wide range of nonlinear problems [8,9]. To protect against convergence to a local minimum rather than the global minimum and against convergence that may be slow or not attained at all, some effort in finding good starting estimates is necessary. In our case we determined the initial estimates to the parameters by solving a somewhat simpler model; namely

$$H_{\mathrm{WC\text{-}Co}}(\alpha_0; d, \lambda) = \alpha_2 d^{\alpha_3} \lambda^{\alpha_4}. \tag{3}$$

Subsequently α_1 is obtained either by adjusting the fit to the data or on the basis of some physical argument. Eq. (3) can be solved to obtain the estimates of $\alpha_2,\ \alpha_3,\ \alpha_4$ via the linear regression analysis procedure followed by a minimization procedure for the complete solution of (1). We used the Lower–Upper decomposition method (LU decomposition method) for the linear regression analysis and the Levenberg–Marquardt method for minimization. Applying these procedures to the data, the empirical formula from Eq. (2) was obtained to be

$$H_{\mathrm{WC\text{-}Co}} = 177.05 + 140.15 d^{0.251} \lambda^{-0.497}. \tag{4}$$

Using (4) the hardness $H_{\mathrm{WC\text{-}Co}}$ is calculated and compared with our data. The results are plotted in Fig. 1. To further test this empirical formula we calculate the hardness of WC–Co by using the grain sizes and the mean free path from other researchers [1,4,6,10], see Fig. 2. The fact that $\alpha_3 \approx \frac{1}{4}$ and $\alpha_4 \approx -\frac{1}{2}$ suggests that a theoretical interpretation should be possible.

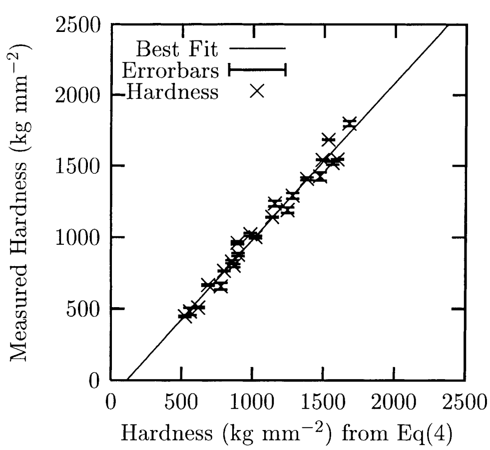

Fig. 1. Measured hardness (our results) vs. empirical formula (Eq. (4)).

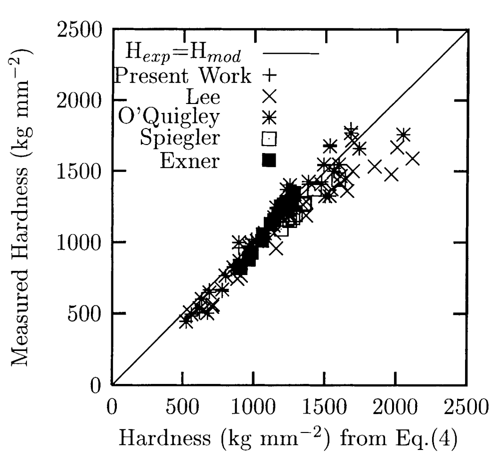

Fig. 2. Measured hardness (various authors) vs. empirical formula (Eq. (4)).

4. Theoretical model

In WC–Co, where Co is the soft phase, dislocations are more easily formed in the cobalt phase than in the WC phase. Of interest in this work is the case where a sequence of dislocations is piled up against an obstacle. The leading dislocation, i.e. the one nearest to the obstacle, experiences an internal stress τ_i given by [11]

$$\tau_i = n\sigma \tag{5}$$

where n is the total number of piled up dislocations of the same sign and σ is the applied stress. When n is large and the stress field at the obstacle is that due to the whole pile-up instead of that of the leading dislocation, the stress at a distance ζ ahead of the pile-up is [12]

$$\sigma(\zeta) \approx \sigma\left(\frac{L}{2\zeta}\right)^{1/2}, \tag{6}$$

where L is the glide plane length and $\zeta \ll L$. In other words, the dislocations packed into a length L of the slip plane produced at a distance ζ ahead of a pile-up a concentrated stress given by Eq. (6).

We shall use the above arguments to present a formalism for the model describing the hardness of WC–Co in terms of the grain size, d, and the mean free path in cobalt, λ. This model assumes a continuous carbide skeleton, therefore it may not apply to soft carbide grades. In WC–Co the dislocation movement in the cobalt phase will be impeded by the WC grains. A WC crystal thus acts as an obstacle. The dislocations will therefore pile-up at the grain boundaries. The length of the pile-up is assumed to be proportional to the mean free path in cobalt or approximately $\frac{1}{2}\lambda$.

Many researchers have shown that WC deforms plastically [13–15]. Nabarro et al. [16] reported that in WC–Co the applied stress is concentrated at the WC necks – the grain boundaries of the carbide phase. Now assume that the length of the cross-section of the grain boundary (neck) between two contiguous carbide crystals is y. Let us consider the sketch in Fig. 3. On one side of the grain boundary of the two contiguous WC grains is a dislocation pile-up of length $\frac{1}{2}\lambda$ in the cobalt phase.

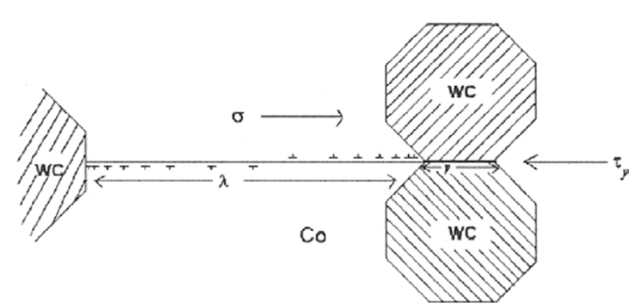

Fig. 3. Schematic representation of the dislocation pile-up in WC–Co.

On the other side τ_y represents the stress that allows shear to propagate along the neck. This figure shows two pile-ups of opposite signs. The one on the left is far from the neck and is moving against a grain and has little effect on the neck. Only the pile-up on the right which is moving against the neck contributes to the force exerted by the dislocations in the cobalt on the neck. Eq. (6) gives the stress arising from the pile-up. The applied stress must be added to this equation. Thus, the shear stress on the glide plane a distance y ahead of a dislocations pile-up of length $\frac{1}{2}\lambda$ is found to be

$$\tau_y = \left[\left(\frac{\lambda}{2y}\right)^{1/2} + 1\right]\sigma. \quad (7)$$

The whole WC–Co material yields when the stress τ_y reaches the flow stress of WC. As German [17] reports the size of the neck between two particles, of a material manufactured by liquid phase sintering, obeys the same laws as those described in [18,19], for a material manufactured by solid state sintering, i.e. $y \propto d^{\beta}$, where the value of β varies with the sintering mechanism but is always close to $\frac{1}{2}$. More generally, we assume that time and temperature are adjusted to give the same degree of sintering. Applying these arguments to WC–Co, which is manufactured by liquid phase sintering [20–22], one may write

$$y \propto d^{1/2}. \quad (8)$$

Hence Eq. (7) reads

$$\tau_y = \left[k\left(\frac{\lambda}{2d^{1/2}}\right)^{1/2} + 1\right]\sigma, \quad (9)$$

where the proportionality constant k has dimensions of the inverse of the fourth root of length. If we make σ the subject of the formula, we get

$$\sigma = \tau_y\left[k\left(\frac{\lambda}{2d^{1/2}}\right)^{1/2} + 1\right]^{-1}, \quad (10)$$

σ is the yield stress of WC–Co since it is the applied stress at which the whole material yields. According to Kelly [23], the yield stress of WC, τ_y, is 690 kg mm^{-2} and if we take into consideration the fact that Vickers hardness is generally related to the yield stress, by HV $\approx$ 3**Y** [24], where **Y** is the yield stress, then the hardness of WC–Co is given by

$$H_{\text{WC–Co}} \approx 3\tau_y\left[k\left(\frac{\lambda}{2d^{1/2}}\right)^{1/2} + 1\right]^{-1}$$
$$\approx 2070\left[k\left(\frac{\lambda}{2d^{1/2}}\right)^{1/2} + 1\right]^{-1}, \quad (11)$$

where k is chosen to fit the data and is found to be 0.56 mm$^{-1/4}$. Fig. 4 shows a comparison between the results obtained using the formalism above and experimental results.

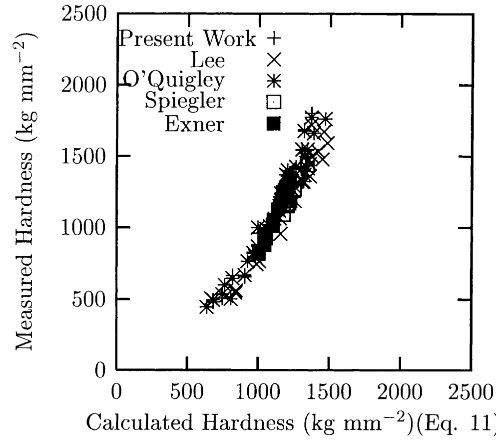

Fig. 4. Experimental hardness (various authors) vs. theoretical model (Eq. (11)).

5. Semi-empirical model

With this model we notice in Fig. 4 that although the lower hardness data are well reproduced, at higher values of hardness, the reproduction is unsatisfactory. Therefore, a further modification to Eq. (11) is necessary. A semi-empirical model is proposed as follows: in order to remove the discrepancy between the theoretical and measured high hardness values, it was found necessary to increase the multiplying factor of the yield stress from 3 to 5.9 leading to a semi-empirical formula for the hardness of WC–Co as

$$H_{\text{WC–Co}} = 4100\left[k'\left(\frac{\lambda}{2d^{1/2}}\right)^{1/2} + 1\right]^{-1} - 130, \quad (12)$$

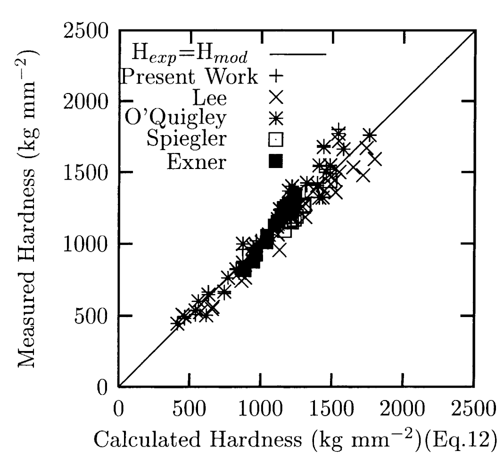

Fig. 5. Experimental hardness (various authors) vs. semi-empirical model (Eq. (12)).

where a value of 130 is subtracted to fit the results. Using this semi-empirical formula with the value of k of previous equations modified to $k' = 22.3\ \mathrm{mm}^{-1/4}$ we obtain the results shown in Fig. 5.

6. Discussion and conclusions

In order to justify the assumption that $H_{\mathrm{WC-Co}} \approx 5.9\sigma$ one must consider that Tabor [24] showed that $H_v \simeq 3\mathbf{Y}$ and calculated indentation strains of the order of 8%. However, it has been reported that this strain value is subject to some uncertainty and that plastic strains ranging from 5% to 20% may correspond to hardness indents [25]. Doi et al. [26] reported that for WC–Co composites, the ratio of Vickers hardness to yield stress (at 0.2% strain) varies from 3.2 to 5.3 depending on the composition and particle size. Therefore, a factor of 5.9 is close to Doi's results. In other words it is plausible to take $H_{\mathrm{WC-Co}} \simeq 6\sigma$. By introducing this relationship, our model is quite successful in reproducing the experimental data and correlating other researchers' results. Work done on the hardness testing of hardmetals showed that testing with different apparatus and different operators can give a variation of ± 50 HV in the average Vickers hardness for the same test piece [6]. Thus, the scatter in the results in Fig. 5 also appears acceptable particularly if one considers that other factors such as binder composition and grain size distribution affect the hardness value. Taking this into account it is reasonable to conclude that our model fits well the experimental results.

Acknowledgements

The authors are grateful to the National Research Foundation of South Africa for financial support.

References

[1] Lee HC, Gurland J. Mater Sci Eng 1978;33:125.
[2] Nabarro FRN, Luyckx SB. In: Proceedings of the International Conference on the Strength of Metals and Alloys. Trans Jpn Inst Met 1968;9:610.
[3] Doi H, Fujiwara Y, Miyake K. In: Proceedings of the International Conference on the Strength of Metals and Alloys. Trans Jpn Inst Met 1968;9:616.
[4] Fischmeister VH, Exner HE. Arch Eisenhüttenwes 1966; 37:499.
[5] Exner HE. Int Met Rev 1979;(4):149.
[6] O'Quigley D. MSc Dissertation, University of the Witwatersrand, 1996.
[7] International Organisation for Standardization, Ref. No. ISO 3878 – 1983 (E).
[8] Press WH, Teukolsky SA, Vetterling WT, Flannery BP. Numerical Recipes in Fortran. Cambridge: Cambridge University Press; 1992.
[9] Gershenfeld N. The nature of mathematical modelling. Cambridge: Cambridge University Press; 1999.
[10] Spiegler R, Schmauder S, Sigl LS, J Hard Mater, 1990;1.
[11] Eshelby JD, Frank FC, Nabarro FRN. Philos Mag 1951; 42:351.
[12] Nabarro FRN. J Less-Common Met 1985;144:59.
[13] Takahashi T, Friese EJ. Philos Mag 1965;2:1.
[14] Bartolucci S, Schlössin HH. Acta Metall 1966;14:337.
[15] Lewis D, Porter LJ. J Appl Cryst 1969;2:249.
[16] Nabarro FRN, Vekinis G, Luyckx SB. Mater Sci Eng 1988;A105/106:337.
[17] German RM. Sintering Theory and Practice. New York: Wiley; 1996. p. 282.
[18] Exner HE, Arzt E. In: Cahn RW, Haasen P, editors. Physical Metallurgy. Amsterdam: North-Holland; 1996. p. 2627.
[19] German RM. Powder metallurgy science. Princeton, NJ: MPIF; 1989.
[20] Kim S, Park JK, Lee D. Scr Mater 1998;38(10):1563.
[21] McHugh PE, Riedel H. Acta Mater 1997;45(7):2995.
[22] Hinnüber J, Rüdiger O. Cobalt 1963;(19):57.
[23] Kelly A. Strong Solids. Oxford: Oxford University Press; 1973.
[24] Tabor D. The Hardness of Metals. Oxford: Oxford University Press; 1951.
[25] Sigl LS, Exner HE. Mater Sci Eng 1989;A108:121.
[26] Doi H, Fujiwara Y, Miyake K. Trans Met Soc AIME 1969;245:1457.