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Quantitative relationships between magnetic properties, microstructure and composition of WC–Co alloys

A. Love [a,c], S. Luyckx [b,c], N. Sacks [b,c,*]

[a] School of Mathematics, University of the Witwatersrand, Private Bag 3, WITS, 2050, South Africa
[b] School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag 3, WITS, 2050, South Africa
[c] DST/NRF Center of Excellence in Strong Materials, South Africa

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ABSTRACT

A quantitative relationship between WC grain size, Co content and coercivity has been derived using data from a wide range of WC–Co alloys. The relationship has been found to agree with data from independent investigations.

1. Introduction

Measurements of magnetic saturation and magnetic coercivity are used in the WC–Co industry to assess the quality of the material (e.g. [1]). The magnetic saturation is used to assess the tungsten (W) concentration in the cobalt (Co) binder and the overall carbon (C) content of the WC–Co alloy, while the coercivity is used as an indirect assessment of WC grain size.

The magnetic saturation provides quantitative information on W concentration in the binder and overall C content, while the coercivity has been providing only qualitative information on WC grain size. The reason being that while the magnetic saturation of WC–Co of known Co content depends only on the W concentration in the binder (which is related to the overall C content) the coercivity does not depend only on WC grain size but also on the W content (e.g. [2]) and the residual stress distribution [3] in the binder.

The relationships between magnetic saturation and composition, which are most commonly used in the WC–Co industry are the following [4,5]:

$$\sigma - \sigma_0 = -8m_{\mathrm{W}} \times 10^{-7} \tag{1}$$

where m_{W} is the at% W in the cobalt binder, σ_0 the magnetic saturation of the material if the binder was pure cobalt, and σ is the measured magnetic saturation of the material being tested, in $\mathrm{T\,m^3/kg}$; and

$$\frac{\mathrm{d(C\,wt\%)}}{\mathrm{d}S} = 0.074(\mathrm{Co\,wt\%}) \tag{2}$$

where C wt% and Co wt% are respectively the weight percent of the overall C and Co in the material, and S is the relative magnetic saturation, i.e. the ratio between the measured magnetic saturation of the material and the magnetic saturation that the material would reach if the Co binder was pure. S, therefore, is independent of the unit used.

It would be useful to have a quantitative relationship between coercivity, WC grain size and Co content. The relationships proposed in the literature seldom agree with each other, although most investigations were carried out using the same techniques, namely, the procedure recommended in the International Standard ISO 3326 for the measurement of the coercivity and linear analysis for the measurement of WC grain size. However, after measuring the linear WC grain intercepts some researchers assumed the mean grain size to be the arithmetic mean linear intercept (e.g. [6]), others assumed it to be the median of the linear intercept size distribution (e.g. [7]) and others did not specify the method adopted.

Therefore the main reason for the lack of agreement may be the different methods of computing the mean grain size, although other possible reasons are the different ranges of WC–Co grades investigated (e.g. [6,8]) or different overall C content in the materials.

For the present investigation the wide range of WC–Co grades available had been produced specifically for the investigation, with

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[*] Corresponding author at: School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag 3, WITS, 2050, South Africa.
E-mail address: Natasha.Sacks@wits.ac.za (N. Sacks).

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Table 1
Grain size, cobalt content, coercivity and magnetic saturation of the grades used in this investigation.

Grade	D_{WC} (μm)	K (kA/m)	MS ($\times 10^{-7}$ T m^3/kg)	Grade	D_{WC} (μm)	K (kA/m)	MS ($\times 10^{-7}$ T m^3/kg)	Co (wt%)
				F4	1.30	23.8	68.7	4
UF6		40.8	82.8	F6	1.27	21.5	121.2	6
UF8		37.0	113.1	F8		19.5	157.6	8
UF10	0.60	31.5	151.5	F10	1.07	18.6	193.9	10
UF12	0.62	26.0	204.0	F12		16.4	232.3	12
UF14	0.59	22.5	236.3	F14	1.17	15.8	274.7	14
UF16	0.65	18.3	317.1	F16		14.7	313.1	16
UF18		17.1	355.5	F18		13.1	353.5	18
UF20	0.56	15.6	395.9	F20	0.96	12.0	397.9	20
UF30	0.66	9.7	591.9	F30	0.84	9.0	593.9	30
UF40	0.61	7.3	791.8	F40	0.86	7.0	791.8	40
UF50	0.56	6.8	997.9	F50	0.96	5.5	985.8	50
M4		15.6	76.8	C4	5.10	8.9	78.8	4
M6	2.66	12.7	111.1	C6	5.32	7.5	117.2	6
M8	2.65	11.1	153.5	C8	5.21	6.5	151.5	8
M10	2.60	10.1	193.9	C10	4.77	6.3	195.9	10
M12	2.97	8.2	214.1	C12	4.89	5.8	234.3	12
M14		7.6	268.7	C14	5.88	5.4	276.7	14
M16		6.7	321.2	C16	5.10	5.2	307.0	16
M18	3.47	6.0	349.5	C18	5.65	4.9	343.4	18
M20		5.3	404.0	C20	5.08	4.8	385.8	20
M30		4.6	585.8	C30	4.86	4.6	585.8	30
M40	3.34	4.0	783.8	C40	4.13	4.0	779.7	40
M50	3.27	3.3	979.7	C50	4.71	3.3	969.6	50

particular attention to the C level [9]. Once it was found that the coercivity results obtained from these grades agreed almost perfectly with independent results obtained by Daub et al. [10] for equivalent grades (i.e. grades of the same Co content and the same WC grain size), it was assumed that the results could be used to derive a quantitative relationship between coercivity, grain size and Co content. Despite the almost perfect agreement with Daub et al.'s results (the C content of whose grades is not known [10]), the effect of variations in C content on the relationship that was derived, was also investigated.

2. Methods

The grain size was measured by linear analysis as described by Exner and Hougardy [11]. The mean WC grain size was calculated as the ratio of the WC volume fraction to the number of WC linear intercepts per unit length. The magnetic saturation was determined using a LDJ saturation induction measuring system type SM 8100 and the coercivity was measured following the International ISO Standard 3326 [9]. As prescribed by the Standard, the coercivity results were rounded to the nearest 0.1 kA/m.

Although the magnetic saturation was not a subject of this investigation because relationships between magnetic saturation and composition are already available in the literature (see Eqs. (1) and (2)), the average magnetic saturation of all grades was measured in order to establish the average overall C content of each grade.

The WC–Co grades used in this investigation are listed in Table 1. The Co content ranged from 4 to 50 wt% and the mean WC grain size from ~0.6 to ~5.0 μm. The grades were divided into 4 groups on the basis of their mean grain size, as shown in Table 2.

The grain size taken as typical of each group of grades is the average of the grain size of the grades in each group (given in Table 1), but the mean grain size of each grade was used when deriving relationships between coercivity and the inverse grain size.

The coercivity results were plotted against Co content at constant WC grain size and against grain size at constant Co content. The equations for the curves obtained were derived using standard data analysis packages.

Table 2
Groups into which the grades in Table 1 were divided on the basis of their mean WC grain size.

Groups of grades	Mean WC grain size (μm)
UF (ultra fine)	0.6 ± 0.04
F (fine)	1.1 ± 0.18
M (medium)	3.0 ± 0.37
C (coarse)	5.1 ± 0.44

3. Results and discussion

Fig. 1 shows the average magnetic saturation of the grades tested as well as the maximum possible magnetic saturation value for each grade and the minimum possible value at which the materials are free from eta phase. Eta phase is a double carbide that is present in the sintered hardmetal when the carbon content is less than the required stoichiometric 6.13 wt%. The maximum possible magnetic saturation corresponds to the case of WC–Co with a pure Co binder (i.e. a binder without W and C in solution) but it may also correspond to WC–Co containing free carbon (e.g. [5]). The presence of free carbon cannot be detected by magnetic saturation measurements. The minimum possible magnetic saturation is assumed to correspond to 80% of the maximum value (although other authors put the minimum at 78% [12] or even 75% [5] of the maximum value) because it was found that below 80% of the maximum magnetic saturation, the overall C content in the material is low enough for eta phase to start being detected [13]. Fig. 1 indicates that most of the grades had a magnetic saturation close to the maximum value; therefore the overall C is close to the stoichiometric content. Metallographic examinations did not reveal any free carbon in the materials. The few grades with a magnetic saturation below the minimum value were grades with low Co content and ultrafine grain size. The average magnetic saturation of the grades tested varied linearly with Co content and did not depend on grain size, as it was expected from the definition of magnetic saturation.

Fig. 2 confirms that the coercivity of WC–Co is a function of both cobalt content and grain size. The trend of the curves in Fig. 2 is in agreement with trends reported in the literature (e.g. [6]), but the individual data agree only with some of the published data (e.g. [10,14]). At high Co contents the coercivity tends to converge to a value between 3 and 6 kA/m that appears to be independent from WC grain size. This must correspond to the coercivity of the binder, which is higher than the coercivity of pure cobalt (~1 kA/m) due to W and C in solution.

Fig. 3 shows that the coercivity increases linearly with the reciprocal of the WC grain size. This trend has already been observed by previous investigators (e.g. [2,6]), although their data exhibited a larger scatter than the present ones.

The equations of the straight lines in Fig. 3 are given in Table 3. In order to establish a quantitative relation-

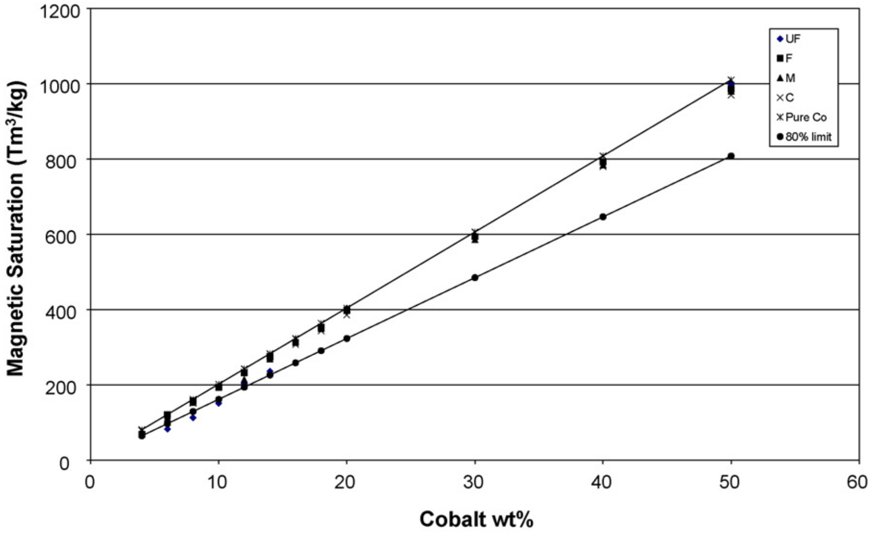

Fig. 1. Magnetic saturation vs. cobalt wt% for the grades listed in Table 1. The upper full line joins points representing the maximum possible values of magnetic saturation at the given cobalt contents while the lower full line joins points representing 80% of the maximum values.

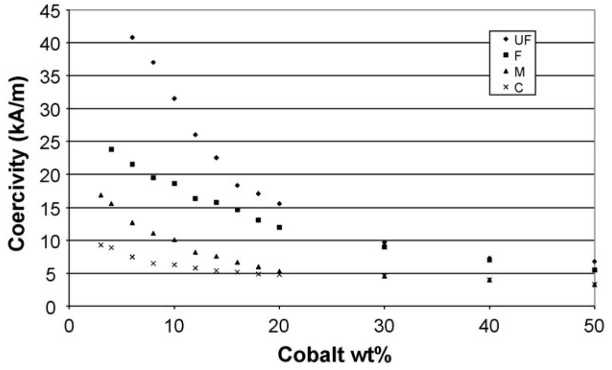

Fig. 2. Coercivity vs. cobalt wt% for each of the grades listed in Table 1. Each set of data corresponds to grades of approximately equal grain size, as indicated in the key.

ship between grain size, coercivity and cobalt content only grades which had at least 3 data points as seen from Fig. 3, were used. The selected grades are reflected in Table 4.

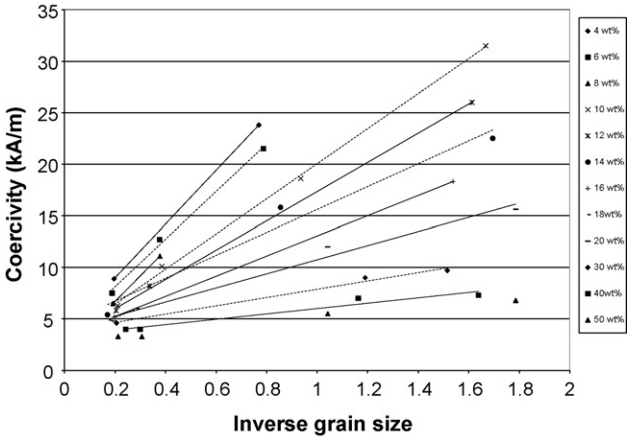

Fig. 3. Coercivity vs. inverse WC grain size for the grades listed in Table 1. Each line is the best fit through points corresponding to grades of equal Co content, as indicated in the key.

Table 3
Equations and regression coefficients for the straight lines in Fig. 3. The inverse WC grain size (in $(\mu m)^{-1}$) is indicated as ‘x’ and the coercivity (in kA/m) as ‘y’.

Co (wt%)	Equation	R^2
4	$y = 26.003x + 3.8033$	1.000
6	$y = 23.053x + 3.5184$	0.9959
8	$y = 24.865x + 1.7259$	1.000
10	$y = 17.022x + 3.0199$	0.9987
12	$y = 14.181x + 3.1513$	0.9995
14	$y = 11.093x + 4.5093$	0.9669
16	$y = 9.7615x + 3.2867$	1.000
18	$y = 9.9099x + 3.1459$	1.000
20	$y = 6.8355x + 3.9075$	0.9766
30	$y = 4.030x + 3.8562$	0.9871
40	$y = 2.6078x + 3.3956$	0.9504
50	$y = 2.3374x + 2.7698$	0.984

The slope ‘s’ of the lines was plotted against the Co content of the grades, as shown in Fig. 4. The relationship between the slope ‘s’ and the Co content from Fig. 4 was found to be:

$$s = 236.7\,(\mathrm{Co\,wt\%})^{-1.2} \tag{3}$$

where the regression coefficient R^2 is 0.9826 and the units of s are kA/m per unit Co wt%.

The intercepts with the coercivity axis of the straight lines in Fig. 3 for the selected grades vary between 2.8 and 4.5 kA/m with a mean value of 3.5 ± 0.6 kA/m. Therefore the relationship between coercivity (H_c), Co wt% and WC grain size (d) has been found to be:

$$H_c = \frac{236.7\,(\mathrm{Co\ wt\%})^{-1.2}}{d} + 3.5 \tag{4}$$

where H_c is in kA/m and d in μm.

Table 4
Grades selected for establishing relationship between coercivity, WC grain size and Co content.

Co (wt%)	Equation	R^2
6	$y = 23.053x + 3.5184$	0.9959
10	$y = 17.022x + 3.0199$	0.9987
12	$y = 14.181x + 3.1513$	0.9995
14	$y = 11.093x + 4.5093$	0.9669
20	$y = 6.8355x + 3.9075$	0.9766
30	$y = 4.030x + 3.8562$	0.9871
40	$y = 2.6078x + 3.3956$	0.9504
50	$y = 2.3374x + 2.7698$	0.984

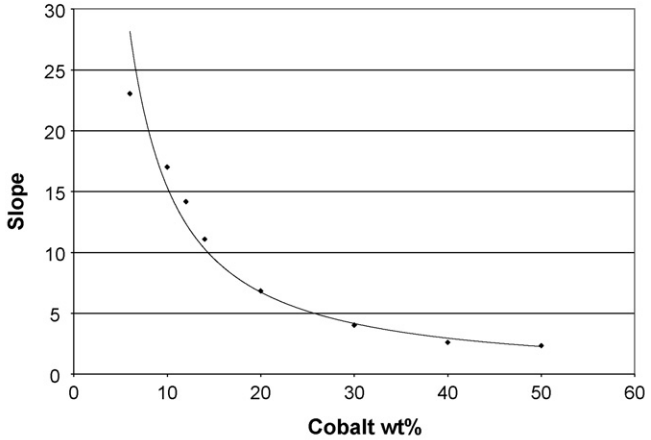

Fig. 4. Slope of the straight lines in Fig. 3 for selected grades vs. cobalt wt%.

Thus the grain size of a grade of known cobalt content can be derived from coercivity measurements using the following equation:

$$d = \frac{236.7\,(\mathrm{Co\ wt\%})^{-1.2}}{H_c - 3.5} \qquad (5)$$

where, again, H_c is in kA/m and d in μm.

Eq. (5) was obtained from all the data in Table 1, including data from grades with magnetic saturation close to, or below, the minimum (see Fig. 1), i.e. grades with C content lower than the average C content of the grades tested. When excluding the grades of magnetic saturation below the minimum the coefficient 236.7 changed to 232.5, the exponent (that was rounded to the nearest decimal figure as −1.2) changed from −1.188 to −1.183 and the constant 3.5 changed to 3.1.

Therefore, the constants appearing in Eq. (5) are not strongly affected by variations in C content within the range of C contents of the grades used in this investigation and the following equation can be used to obtain with good approximation the WC grain size of all the grades investigated:

$$d = \frac{235\,(\mathrm{Co\ wt\%})^{-1.2}}{H_c - 3.3} \qquad (6)$$

for the same units as in Eq. (5).

Eq. (6) has been applied to many of the data reported in the literature. Excellent agreement has been found between Eq. (6) and Daub et al.'s data [10] (for ultrafine grades the calculated grain size differed from the reported grain size by 0.04 μm, for fine grades by 0.05 μm and for medium grades by 0.2 μm) and Porat and Malek's data [14] (again the difference ranged from 0 to 0.2 μm).

However, in the case of other data published in the literature (e.g. [6,8]) the agreement was not good. Besides the possible reasons that have been mentioned earlier, an additional reason for the lack of agreement is that the quoted cobalt content may not have been the actual cobalt content of the grades. For example Topić [7] showed by X-ray fluorescence that the cobalt content of some of the grades differed appreciably from the Co content quoted by the suppliers. Another example is given by the data in [6], since not only the reported coercivity but also the reported hardness seem to be too low for the quoted Co contents and grain sizes.

Among the relationships between coercivity, composition and microstructural parameters of WC–Co found in the literature, the closest to Eq. (6) is an equation of similar form proposed by Pärnama et al. [15]. This was found to give results close to the data by Daub et al. [10] and Porat and Malik [14] but less close than the results obtained by applying Eq. (6).

Eq. (6) consists of an exponent −1.2 (or 1.188 to be precise). Some researchers may consider an exponent of exactly −1 to be 'more natural' for the derived relationship. To consider this idea, an exponent of −1 was inserted into Eq. (6) and the associated graphs generated. The correlation coefficient for the generated relationship was found to be $R^2 = 0.9654$. Although this coefficient is deemed to be acceptable it is not as good as the coefficient determined using the actual data points, i.e. $R^2 = 0.9826$ which generated a coefficient of −1.188.

4. Conclusions

This investigation has shown that it is possible to use coercivity results to calculate the mean grain size of WC–Co grades of known Co content to an approximation of 5–10%. The relationship presented in this paper (Eq. (6)) appears to be generally applicable since it has been found to agree with many independent results published in the literature (e.g. [10,14]).

The coercivity of WC–Co is known to depend on the overall carbon content of the material (e.g. [2]). However, the general applicability of the relationship presented in this paper (i.e. the fact that the relationship is applicable to grades of unknown C content and from different producers) indicates that the C content does not affect the coercivity as strongly as the Co content and the WC grain size.

Since the residual stress distribution strongly affects the coercivity of WC–Co [3], Eq. (6) is only applicable to unused components and not to components that have been subjected to external stresses in service.

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