

Measurement Note

Magnetic Coercivity Measurements for WC/Co Hardmetals

Summary

Magnetic coercivity measurements are used by the hardmetal industry for non-destructive quality control. In two phase WC/Co hardmetals coercive force is proportional to the interface area between the Co binder-phase and the WC hard phase. The interface area is related to the WC grain size and thus measurements of coercive force are an indirect method for monitoring this parameter. This Measurement Note summarises the background to the use of this technique and uses recent direct measurements of grain size on a wide range of WC/Co hardmetals to develop the concept of a property map relating coercivity to WC grain size. The issues covered are:

- Background to magnetic measurements
 - sources of uncertainty
 - composition, residual stresses, contiguity
- Industrial drivers for grain size measurements
 - Terminology for grain size distribution
- Grain size measurement
 - Models and Validation
- Property Maps

It was concluded that coercivity can be used in principle to predict grain size but agreement is needed on a standardised method to define grain size.

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Background

The composition of WC/Co hardmetals is conventionally specified in terms of how much Co is present in wt% and a nominal figure for the grain size of the WC. The amount of alloying elements (W and C) present in the Co binder-phase can, in principle, be determined by measurements of magnetic properties such as coercivity and saturation magnetisation (magnetic moment) and methods exist to measure these properties. But, measurement of the WC grain size is not standardised. The required methods are not straightforward and this is particularly the case for very fine grained materials. The results of grain size measurement methods frequently depend on the method of preparation and examination of samples^{1,2}.

There is no widely agreed non-destructive method for measurement of grain size, although coercivity is often used empirically. Coercivity is the magnetic field required for complete demagnetisation of a fully magnetised hardmetal testpiece (Fig 1). The method is specified in an international standard, ISO 3326 (Hardmetals - determination of coercivity).

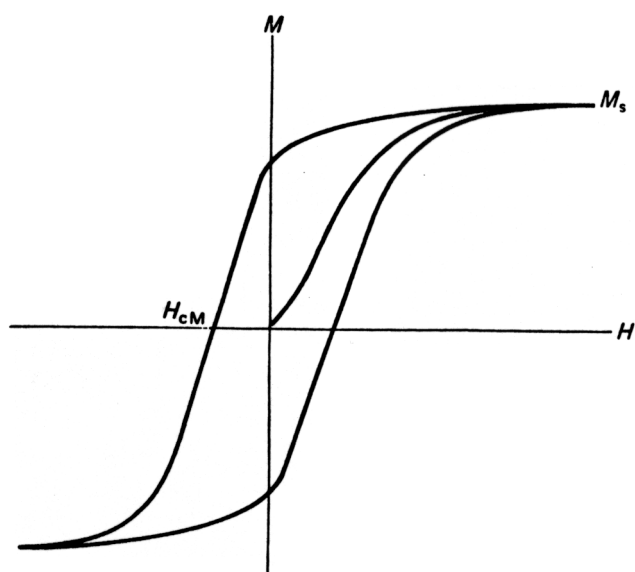


Fig 1 Schematic diagram of magnetisation curve showing coercive force.

The coercive force required to demagnetise a WC/Co hardmetal is primarily related to the Co/WC interphase area, because magnetic domain walls are pinned by these phase boundaries. The Co/WC interphase area is inversely related to the WC grain size. For smaller values of the latter the interphase area increases and consequently so does the coercivity. However, coercivity may also change with change in Co composition and this should be allowed for in empirical equations relating WC grain size to coercivity. Furthermore, difficulties may arise when trying to correlate coercivity with grain size due to the effects of differences in cooling rate from the sintering temperature, that can result in changes to the composition of the binder phase. For example, in low carbon content hardmetals it is possible to precipitate Co₃W in the binder phase on ageing of the hardmetal after accelerated cooling. This procedure results in very significant changes in coercivity. Additionally, there may be effects on coercivity due to the phase boundaries between the hexagonal and face centred cubic phases in individual binder regions. Also, it is well known that deformed hardmetals show a significant increase in coercivity due to deformation of the binder phase, i.e. creation of phase boundaries, twins and stacking faults, which can be reduced on subsequent annealing. Finally, the role of WC/WC contiguity must also be acknowledged since it can be seen that two materials of different contiguity but similar grain size will have different interphase areas, and hence different coercivities.

Thus, in principle coercivity can be used as a non-destructive examination technique to estimate WC grain size, but it is important to be aware of factors such as:

- compositional variation
- structure modification
- cooling rate effects
- deformational stresses

all of which can affect the measured value of coercive force.

Industrial Drivers

A major driving force for the development of hardmetals with ever finer WC grain sizes is the belief that hardness generally increases with a decrease in grain size. Furthermore, it has been reported³ that the toughness (Palmqvist) of

'nanograined' hardmetals is greater than would be expected for a given level of hardness. However, other publications⁴ have shown that, even though hardness does increase as the grain size decreases, plane strain fracture toughness may approach an asymptotic value equivalent to the WC/WC interface toughness of about 6-7 MN m^{-3/2}.

At present it is difficult to reach firm conclusions regarding the changes in properties that obtain from the introduction of finer grained hardmetals because, in general, non-standard test methods are used and it is difficult to compare data. Even for hardness measurements where microhardness, Rockwell and conventional Vickers values have been quoted, none of these test methods are easily comparable.

Terminology

A very wide range of terms are used to describe powders or sintered hardmetals of different grain sizes. For example, the following have been used in a number of publications and reports

Extra coarse	Fine	Microfine
Coarse	Very fine	Micrograin
Coarse/medium	Ultra-fine	Nanophase
Medium	Extra fine	Nanograin
Medium/fine	Submicron	Super fine

None of these terms have commonly agreed or well defined size ranges among users and producers of powders and sintered products. However, locally, organisations, groups or manufacturers have developed in-house definitions. Unfortunately, although there is some overlap, in general these in-house definitions do not have a one-to-one correspondence.

Clearly to prepare a scheme which rationalises the use of the various terms will be inconsistent to a degree with at least some existing in-house schemes. Additionally, existing usage might present problems if it was felt that a proposed terminology did not acknowledge terms felt to be widely understood by customers. However, perhaps there is a place for more idiomatic phrases to be used in marketing alongside a well defined and logical framework to be used for technical purposes.

A more intransigent problem is that of a definition for the size and/or distribution of the WC, either as a powder or in the hardmetal. There is as yet no standard available and a terminology scheme must take this into account. For example, powders are available with mean sizes expressed as particle diameters in 3-D; furthermore the mean value is given as the mean of the mass distribution of the batch. By contrast, the most commonly used method to measure the size of WC grains in a sintered product is the linear intercept technique where the mean value is expressed as the arithmetic mean of the number distribution on a 2-D image. It has been shown for lognormal distributions⁵ that the difference in geometric mean between number and mass is given by $3\sigma^2$ where σ is a measure of the distribution width. Typically σ has a value of 0.3 and since the antilog of $3\sigma^2$ is required to ascertain the shift between number and mass the shift can be very large, especially for grain sizes less than 1 μm . The following example can be used to illustrate the problem.

Consider a sintered hardmetal with an arithmetic mean linear intercept (2-D) for the WC of 0.6 μm . For a typical distribution⁵ with a σ of about 0.3 the geometric mean would be about 0.5 μm . Assuming a multiplication factor of about 1.5 to convert from 2-D to 3-D this gives a mean particle diameter by number of 0.75 μm which is equivalent to a geometric mean by mass of antilog ($\log 0.75 + 3\sigma^2$), i.e. 1.0 μm . To put it another way an intercept distribution measured on an as-received powder might give an arithmetic mean linear intercept of about 0.6 μm from a powder sold with a mean particle diameter of 1.0 μm on a mass basis, assuming no substantive change in diameter occurs in the sintering process.

Grain size measurement

The most direct way to measure the WC grain size⁶ is to polish and etch a cross-section of the microstructure and then use quantitative metallographic techniques to obtain a mean value for the grain size either by point or area counting, by linear intercept techniques (Heyn method) or by measurement of the number of grains per unit area (Jeffries method). This can be performed using optical microscopes for some coarser-grained WC hardmetals but for many materials the

grain size is too fine to be resolved optically and so scanning electron microscopes (SEM) must be used^{1,2}. In very fine grained hardmetals the average grain size can be very small, less than 0.5 µm for the arithmetic mean linear intercept, and good quality images are difficult to obtain in conventional SEMs.

For the purpose of the present evaluation the grain size and size distributions of a range of WC/Co hardmetals were measured manually using the linear intercept method. A straight line was drawn across a micrograph of the structure and the length of line crossing each WC grain constituted one value of the linear intercept. For each hardmetal 300–400 grains were measured to give a representative average value for the intercept lengths.

Models and Validation

Models have been developed to relate coercivity to WC grain size, where some are physically based and some are empirically based. A model which is physically based is used at NPL and this has been validated by careful measurements of WC arithmetic mean linear intercept. The major source of discrepancy between models is likely to be due to differences in the definitions and measurement methods used for grain size.

Several equations have been reported^{3,8-10} which relate coercivity to grain size and these have been critically examined in comparison with linear intercept grain size measurements made at the National Physical Laboratory (NPL)¹¹.

In general WC grain size, d , was not well defined but has been assumed to be the arithmetic mean linear intercept in the following expressions. The relevant equations are given by Porat and Malek⁸

$$d = 0.3 (80 / K)^{0.57(1/V_{Co})^{1/3}} \quad (1)$$

by Cheney et al⁹ as

$$\log d = I_1 - mK \quad (2)$$

and by Fang and Eason⁴

$$d = 73(1 - 1.03 \exp[-5 V_{Co}]) \left(\frac{1 - V_{Co}}{KV_{Co}} \right) \quad (3)$$

by Exner and Fischmeister¹⁰

$$d = (1 - k) (73 / K) ((1 / V_{Co}) - 1) \quad (4)$$

where k is the contiguity of the WC skeleton, which is a measure of the interparticle WC/WC contact area. Also, V_{Co} is the cobalt volume fraction, K is the coercivity and I_1 and m are constants. Equation (3) appears to be similar to eqn (4) where the contiguity k is replaced by the expression $1.03 \exp[-5 V_{Co}]$. For hardmetals with 6 wt.%Co binder phases (approximately 10 vol.%Co) these equations reduce to

$$d = 3770/(K)^{2.154} \quad (5)$$

$$\log d = 1.778 - 0.0076K \quad (6)$$

$$d = 247/K \quad (7)$$

$$d = 243/K, \text{ for } k = 0.63$$

where K , the coercivity, is in oersteds.

To change oersteds to kA m⁻¹ (the appropriate SI unit) the value in oersteds must be divided by 12.57.

The value of 0.63 for k for eqn (8) was obtained using the following relations

$$d_{wc} = d_{Co}(1 - k) \left(\frac{1 - V_{Co}}{V_{Co}} \right), \text{ with } V_{Co} = 0.1 \quad (9)$$

and

$$d_{Co} = 0.3 d_{wc}$$

where d_{Co} is the mean linear intercept in the Co phase.

Equation (9) is the quantitative expression inter-relating d_{Co} , d_{wc} , V_{Co} and contiguity. Equation (10) is an empirical equation obtained in work at NPL (see below)⁶.

Equations (5)-(8) are clearly different and some appear to be empirically based. However, it is possible to derive a physically based model which relates coercivity to grain size. This model must be considered a first approximation because it does not take into account all the compositional effects which can affect coercivity that were discussed previously. A linear relation between coercivity and grain size is a result of the effect of the WC/Co interphase area per unit volume, I_A , on coercivity¹⁰. Interfaces between WC and Co pin domain walls and thus have a direct influence. I_A can be derived from quantitative metallography¹².

$$I_A = \frac{2}{d} \quad (11)$$

It has been shown in work at NPL⁶ that for a range of commercial and research hardmetals

$$d_{Co} = d_{WC} (0.1 + 2.0 V_{Co}) \quad (12)$$

where d_{WC} is the arithmetic mean, WC intercept length and V_{Co} is the volume fraction of cobalt. This empirical relation takes account of contiguity between WC grains. It is possible that some of the equations relating grain size, coercivity and cobalt fraction outlined above do not account for this parameter.

Thus for the 6wt% (approximately 10 vol.%)Co materials⁶, if $K \propto I_A$, then

$$K \propto \frac{2}{d}, \text{ i.e. } K \propto \frac{1}{d} \quad (13)$$

Thus

$$K = a + b/d_{WC} \quad (14)$$

The above relations, eqns (5)-(8) and (14), can be summarised, for a constant Co fraction, as

$$\ln d = a_1 - b_1 \ln K \quad (15)$$

$$\ln d = a_2 - b_2 K \quad (16)$$

$$\ln d = a_3 - \ln K \quad (17)$$

$$\ln d = a_4 - \ln K \quad (18)$$

$$\ln d = a_5 - \ln (K - b_5) \quad (19)$$

where a_n, b_n are constants. The expressions of Fang and Exner ((17) and (18)) are similar in form to the NPL equations ((14) and (19)). However, they assume that extrapolation of the data to large values of d gives a value of zero for K , which is not physically realistic. Expressions (14) and (19) extrapolate back to give a positive value for K when $1/d$ is equal to zero. An expression similar to that given by eqn (14) is used at Sandvik with a further modification for different cobalt contents¹³.

These equations were assessed using measurements on a large set of WC/6 wt%Co hardmetals¹¹. There was poor agreement between the different expressions and the most likely source of the discrepancy was in the measurement of grain size used to establish the respective expressions, since this is not a standardised measurement.

For 6 wt%Co/WC hardmetals the relationship between magnetic coercivity and arithmetic mean linear intercept is given in Fig 2, which shows a plot of the coercivity values against grain size. These results can be characterised by a straight line given by expression (14) above where K is the coercivity in kA m^{-1} , a and b are constants and d_{WC} is the WC arithmetic mean linear intercept in μm . The values of a and b are 3.9 and 8.6 respectively. The linear relation is consistent with the arguments given above for a physically based relation between d_{WC} and K .

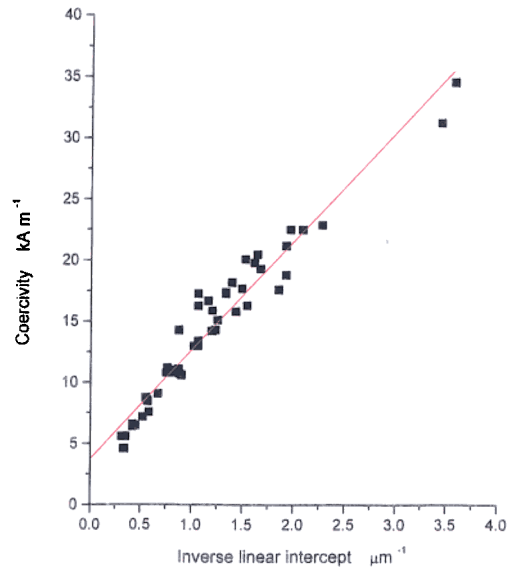


Fig 2 Coercivity/inverse grain size relation in 6wt%Co/WC hardmetals.

the property map was developed assuming a composition approximately in the centre of the two-phase WC/Co region and assuming a conventional WC grain size distribution with the arithmetic number mean intercept, d , as the parameter characterising WC grain size.

The rationale behind the construction of the map was to use grain size (intercept) data from a wide range of WC/Co hardmetals with different Co contents to generate equations relating coercivity to grain size. This equation was physically based as described above.

Many of the additional materials examined had coercivity values within the same range as the 6 wt%Co hardmetals. The coercivity data were grouped into batches based on Co content as follows:

6% 10% 15% 20% 25%

Plots of coercivity versus the inverse grain size are shown in Fig 5 for each group together with a linear fit. The fitted values for the coefficients a and b for each Co group were:

Wt% Co	a	b
6	1.74	10.61
10	2.10	8.63
15	1.89	6.55
20	1.94	5.14
25	2.85	3.53

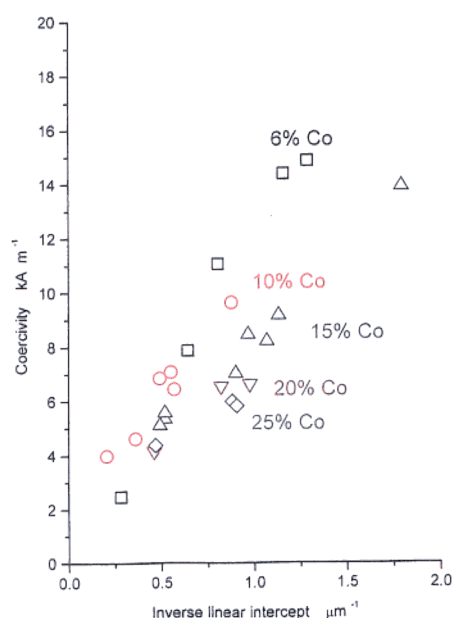


Fig 5 Coercivity/inverse grain size for a wide range of WC/Co hardmetals.

It can be seen that the a and b values for the 6 wt%Co were very similar to those obtained in earlier work³ described above. Because the variation of a and b with Co content is reasonably linear, further analysis allows an expression to be written for the variation of coercivity, K , with grain size, d for $6 < \text{Co wt\%} < 25$ as follows:

$$K = (c_1 + d_1 w_{\text{Co}} + (c_2 + d_2 w_{\text{Co}}) / d) \quad (23)$$

$$\text{where } c_1 = 1.44 \quad d_1 = 0.04$$

$$c_2 = 12.47 \quad d_2 = -0.37$$

with K in kA m^{-1} and d in μm .

Expression (23) can now be plotted as a property map, Figs 6 and 7, bearing in mind the constraint that it has not been extensively validated for coercivity values greater than about 15 kA m^{-1} , ie equivalent to WC grain sizes (arithmetic linear intercept) less than about $0.8 \mu\text{m}$. Additional work is needed to evaluate the finer grained materials. Fig 6 plots expression (23) as $y = a + bx$ with x as $1/d$. Fig 7 plots expression (16) with $x(d)$ as a linear abscissa.

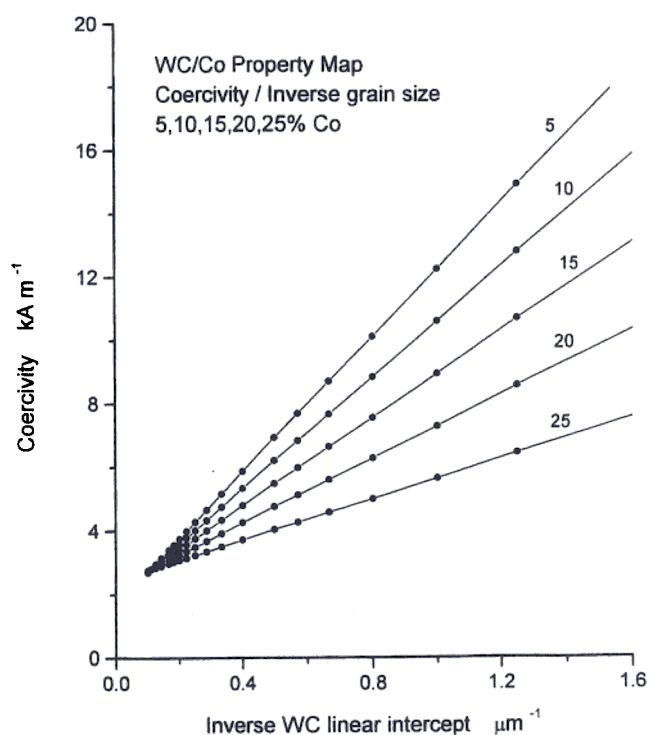


Fig 6 Coercivity/inverse grain size property map.

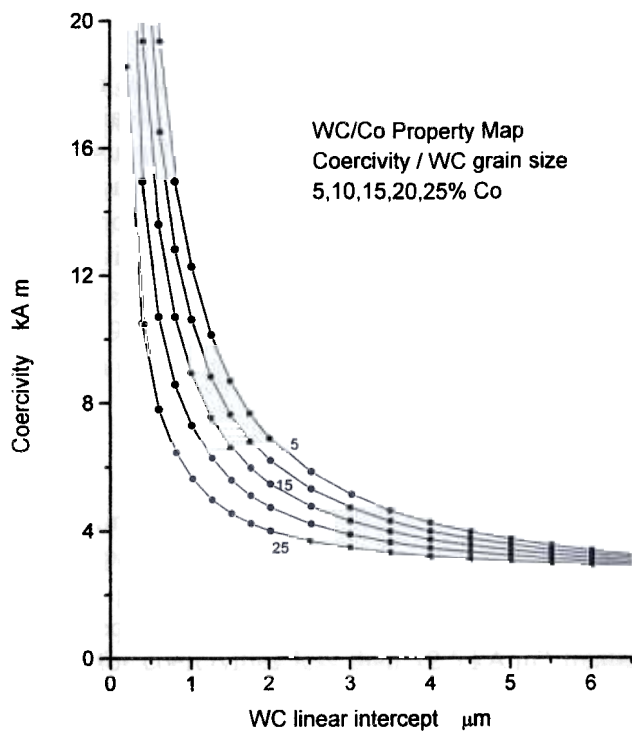


Fig 7 Coercivity/grain size property map.

A property map using wt%Co content as the variable can also be plotted from expression (23). This is shown in Fig 8 for values of linear intercept WC grain size of 5, 2, 1, 0.75 and 0.5 μm , respectively.

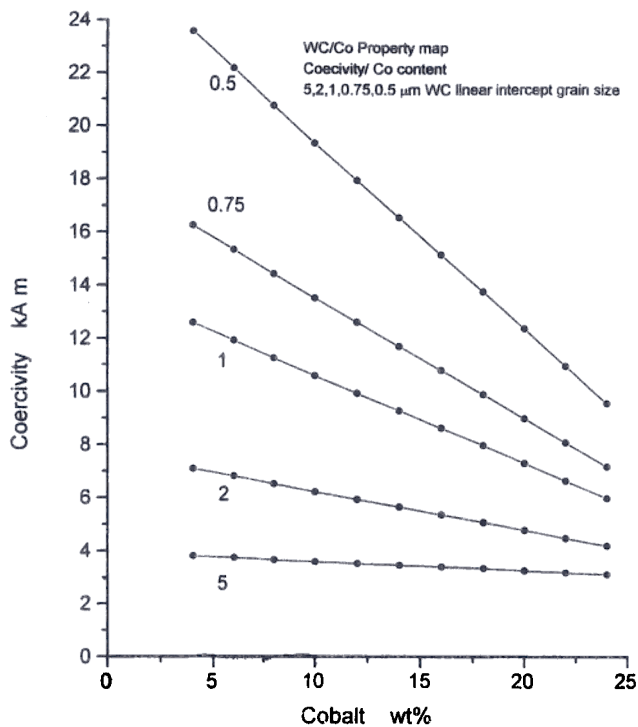


Fig 8 Coercivity/Co content property map.

It is necessary to be aware that the coercivity also varies with carbon content and W content of the binder-phase. The materials contained a range of carbon contents and this has not been allowed for in the construction of the property maps. It has been assumed that the compositions are approximately in the centre of the two phase field. An estimate of uncertainty due to this source can be calculated from measurements of coercivity on materials examined in previous unpublished collaborative work with the British Hardmetal Association Research Group coded BH12C, BH6F and V1. BH12C and BH6F were 12 wt% and 6 wt% Co hardmetals, medium and fine grained respectively. Material V1 was similar to BH6F but contained 2wt% TaC. These materials were manufactured deliberately with a range of carbon contents. The coercivity values across the two-phase field were as follows:

BH6F	20-22 kA m ⁻¹
V1	10-14 kA m ⁻¹
BH12C	9-13 kA m ⁻¹

Expression (23) can be used to calculate a mean WC intercept value of grain size and compared with these measured values as follows:

Code	Calculated WC Grain Size, μm^*	Measured WC mean intercept, μm
BH6F	0.50 - 0.56	0.4 - 0.5*
V1	0.7 - 1.1	1.1
BH12C	0.8 - 1.2	1.1 - 1.4

*Calculated using expression (23)

*Measured using transmission electron microscopy; probably underestimates mean size

It can be seen that the agreement is quite reasonable. The calculated size varies by about $\pm 20\%$ across the two phase field, whereas the measured variation is around $\pm 10\%$. The difference is thus probably due to variation in composition. Further work would be needed to refine expression (23) to allow for this effect.

A further aspect that is clear from inspecting the property maps is that the coercivity measurements are fairly insensitive to changes in grain size as the mean value increases beyond about 3 μm .

CONCLUSIONS

For current commercial WC/Co hardmetals with coercivities less than about 15 mA m^{-1} .

Coercivity can be used in principle to predict grain size but agreement is needed on a standardised method to define grain size.

Experimental materials and new methods of preparation for characterising the structure of very fine grained hardmetals particularly with grain sizes (arithmetic mean linear intercept) in the range of $0.3\text{-}0.1 \mu\text{m}$, but also greater than about $3 \mu\text{m}$, are required to examine the wider applicability of coercivity models for WC/Co hardmetals.

It is also possible that microstructural instabilities in low C hardmetals or residual stresses could affect measurements of coercivity through changes in internal strain and composition. These effects contribute added uncertainty to the correlation between grain size and coercivity and further work is needed to systematically examine these effects.

ACKNOWLEDGEMENTS

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