

REPORT

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Electrical and Magnetic Measurements of Hardmetals with Ni binder phase

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ABSTRACT

Methods of measuring resistivity and magnetic properties on a small scale in hardmetals have been assessed, with particular attention to hardmetals with Ni binders where conventional magnetic property measurement gives little or no information.

The miniaturised four-point probe method can be used to give measurements of resistivity of hardmetal components which do not have a conventional rod or bar geometry. Absolute values can only be obtained by this means from thick samples away from edges, but comparative measurements can be made on any component if the geometry of the probe and component are kept constant. A reference sample should be used to detect drift in values whether absolute or comparative measurements are being made.

Resistivity has been found to correlate well with coercivity in conventional Co binder hardmetals. In Ni binder hardmetals resistivity would appear to discriminate well between samples produced under different conditions where magnetic measurements are not possible. However it has not yet been established what differences in microstructure are being discriminated by these measurements.

As an alternative to the four-point probe, a small eddy current probe has been shown to be capable of measuring differences between hardmetal samples, with very good correlation between the probe inductance and magnetic moment for Co binder hardmetals. With Ni binder materials the eddy current probe output gives information which is complementary to resistivity data and appears to distinguish between materials with different binder phase grain size and WC grain size, but further work is needed on more samples to understand this information fully.

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Approved on behalf of the Managing Director, NPL,
by Dr M Cain, Knowledge Leader, Materials Team
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1 INTRODUCTION

The magnetic properties of WC based hardmetals provide convenient means for non-destructive and relatively quick quality control measurements of components. The most common grades use Co as the binder phase which is strongly ferromagnetic and produces measurable values of coercivity H_c and what is variously described as magnetic saturation B_s or magnetic moment σ . Other elements such as Ni are increasingly being used to replace some or all of the Co and in hardmetals these produce a much weaker ferromagnetic response. This is increasing the requirements to develop alternative non-magnetic measurement methods with better discrimination for quality control.

1.1 MAGNETIC MEASUREMENTS

Magnetic saturation is used as shorthand to describe the maximum magnetic induction produced in a testpiece when held in a fixed magnetic field. It is generally reported either as magnetic moment / unit weight, σ , or magnetic saturation / unit weight, $4\pi\sigma$, and further scope for confusion is added by giving the result in terms of unit weight of the total sample or unit weight of the binder phase only. Roebuck ¹ has summarised the relationship between all these possible results.

In practice most measuring equipment does not produce fields sufficiently strong to fully saturate the Co binder phase and this may lead to minor differences in measurement ^{1,2} between different pieces of equipment, especially at higher Co contents. Magnetic saturation is influenced by the Co content, but for a given Co content in a WC-Co hardmetal the value measured will be reduced in proportion with the percentage of W (or other binder phase additions) in solution. From this concentration of W in Co, the proximity of the sample to the composition boundaries at which free carbon (graphite) forms or at the opposite extreme, eta-phase (or other carbides $M_{12}C$ and M_6C), can be calculated.

Coercivity is a measure of the field required to reduce the flux density within a component from full saturation to zero and this characterises the ease with which the orientation of magnetic domains can be reversed. Reversal is harder where pinning of domains by interfaces or defects is greater and hence finer WC grain sizes produce higher coercivities because of the greater WC/co interface area. However, increased W content of the binder phase also increases coercivity for a given grain size and other phase additions (e.g. grain growth inhibitors) and factors such as stresses from cooling or deformation can alter its value. Because composition and grain size are often interlinked, a correlation between H_c and B_s for a given Co content is often observed.

1.2 MEASUREMENTS IN NI BASED MATERIALS.

Ni can also be used as a binder phase, and on initial consideration it would appear to be suitable for similar measurements of magnetic moment and coercivity, being ferromagnetic, although pure Ni has a saturation magnetisation only 40% that of Co. In practice, the values of magnetic moment in Ni based WC hardmetals are substantially smaller than this reduction would suggest and often are too small to be

measured easily. This is partly because the presence of C in solution in Ni (unlike Co) also reduces the magnetic moment, but it has also been attributed³ to W in solution depressing the Curie temperature which causes an extra decline in the magnetic moment and further complicating the estimation of composition. Measurement of coercivity is similarly difficult or impossible in highly alloyed Ni based binders.

In such cases it may be possible to measure the electrical resistivity of the sample, since this property may be affected by the composition of the binder phase and by the grain size. Roebuck and van den Berg⁴ (1999) summarised the effects of these parameters on Co based materials and showed that the binder phase volume fraction had only a small effect on resistivity, but that decreasing the concentration of C (and thus increasing W) in solution in the binder phase increased resistivity. WC grain size was also thought likely to influence the results but deconvolution of this parameter from C composition made this difficult to quantify. Little has been reported on resistivity in Ni based hardmetals so it is of interest to investigate how resistivity measurements in these materials can be related to the effects of composition and microstructure and whether it can therefore be used in place of, or complementary to magnetic measurements.

1.3 MEASUREMENT OF RESISTIVITY

Resistivity of conductive materials is conventionally measured by a four terminal method on a long bar of material such as rod or strip with uniform cross section A . An electric current, I , is passed through the bar from contacts on the ends and a measurement of the potential drop, V , between two contacts, positioned towards the middle of the sample (at least 1.5x the cross-sectional perimeter from the current contacts) with an accurately known spacing, L , allows the resistance R to be measured from Ohm's Law. Resistivity, ρ , is then calculated from the resistance and the dimensions of the sample between the potential contacts.

$$\rho = R.A / L = (V/I).A / L$$

Reversing the current allows an average to be determined and remove the effects of thermal emfs caused by junctions of dissimilar metals.

In the semiconductor industry the four-point probe is widely used, most commonly with 4 closely spaced point probes, (typically the probe spacing is 1 to 2 mm). This permits measurements from much smaller samples than the standard for conductive materials, and where strip material is not available. However significant corrections are needed when the sample dimensions (thickness, distance from edges) approach that of the probe spacing. For an infinitely large sample, the resistivity is given by:

$$\rho = 2\pi s V/I$$

where s is the spacing between each of the four probes (Figure 2.1).

For finite samples the field around the probes is affected by its interaction with the sample edges and the equation is therefore modified by a correction factor G :

$$\rho = 2\pi s G(s/d, s/t) V/I$$

where d is the distance of the probes from the sample edge and t the sample thickness. For simple geometries G can be calculated and tabulated^{5,6} and various methods have been devised for more complicated geometries⁷. For complex shapes (e.g. curved surfaces, variable thickness), it may be extremely difficult to calculate G but in such cases comparative measurements can still be made if the geometry of probe and samples is held constant.

Resistivity of non-ferromagnetic materials can also be measured by eddy-current methods, in which the change of inductance of a search coil brought to a fixed small distance from the surface material can be related to resistivity of the material. Resistivity of ferromagnetic materials has the same effect, but calculations here are complicated by the magnetic properties of the sample which also influences the change of inductance.

This document assesses measurements made by all three of these techniques on hardmetals, firstly as a means of providing a tool to discriminate between hardmetal grades, and secondly as a means of measuring local property variation by positioning small four-point or eddy current probes at different points on the surface of components.

2 RESISTIVITY – FOUR-POINT PROBE MEASUREMENT

Miniaturised four-point probe measurements were made on a range of hardmetals and compared with conventional measurements of bar samples. Eddy current probe measurements on the same samples are described in a later section. The application of the miniaturised four-point probe to real components is illustrated by a couple of case studies at the end of this section.

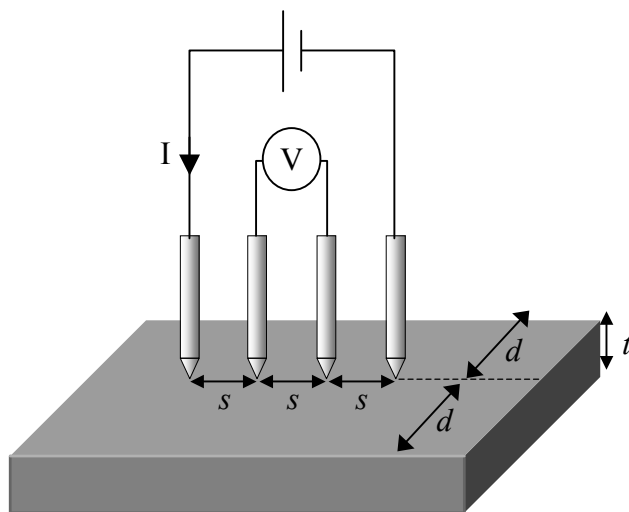


Figure 2.1) Schematic of miniaturised four-point probe

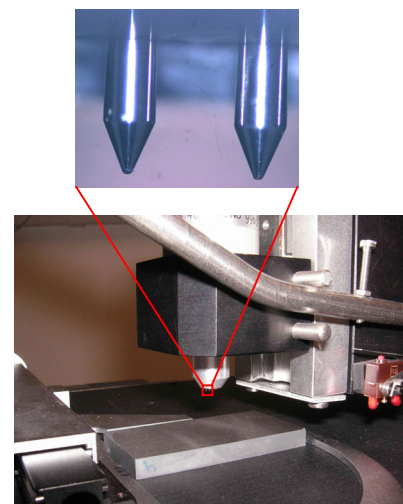


Figure 2.2) Jandel four-point probe

2.1 COMPARISON OF MINIATURISED FOUR-POINT PROBE AND CONVENTIONAL MEASUREMENTS OF RESISTIVITY.

Measurements on hardmetal samples were made with a Jandel miniaturised four-point probe with WC hardmetal probes with spacing $s = 1\text{ mm}$ (Figure 2.1). The four-point probe head is mounted in a lever arm arrangement above an X-Y table on which the sample to be tested is mounted. This ensures that the head was always lowered consistently onto the same point of the sample under test and/or for multiple samples of the same geometry, measurements were made at identical and equivalent positions. The probes are sprung loaded and the mechanical end-stop on the head ensures a constant contact pressure is maintained.

Current was supplied by an HP6030A power supply, and voltages were measured with a Keithley 181 nanovoltmeter. Accurate measurement of the current was achieved by measurement of the voltage across a Tinsley type 1660 standard resistor certified with a resistance of 0.01Ω ($\pm 0.05\%$ maximum error). Repeat measurements were made on each sample by reversing the current. In practice, the greatest source of uncertainties arose from ensuring a stable current supply and measuring the voltage (typically $20 - 50\ \mu\text{V}$) between the probes. Repeat measurements gave an uncertainty of about $\pm 3\%$ ($k = 2$).

For conventional measurements of resistivity on long bars the same circuit was used but contacts for the current were made with sprung clips and voltage measurements were made with sprung loaded gold plated pins.

2.1.1 Effects of Geometry and Correction Factors

Before comparing results of four-point and conventional measurements, it is worth illustrating the effect of size and geometry on resistivities calculated without applying correction factors. Figure 2.3 shows that when the 1 mm spaced probe is brought closer than about 2.5 mm to the edge the uncorrected value rises increasingly rapidly, and conversely the correction factor G must decrease rapidly. Figure 2.3 also shows that reducing the thickness of a sample from 5 mm to 2 mm increases the uncorrected value by approximately 30 %; combinations of thin samples and closeness to edges can easily double the measured values of resistivity.

In general it can be stated that correction factors become significant for (in terms of a 1 mm probe spacing):

$$s/t \leq 1/3.5 \quad \text{and} \quad s/d \leq 1/2.5;$$

for the 2 mm and 5 mm thick samples, correction factors of 0.765 and 0.985 were estimated from published tables and graphs^{5,6}.

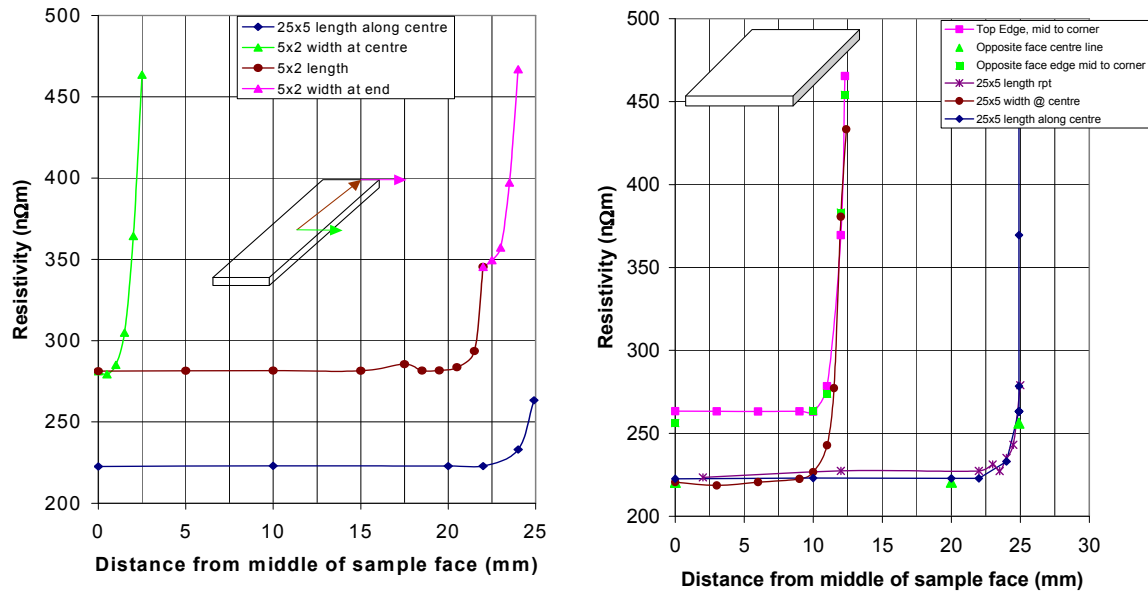


Figure 2.3 Graphs of resistivity ($\rho = 2\pi s V/I$) before correction factors applied. a) for thin bars $25 \times 5 \times 2$ mm with probes aligned parallel to the long axis and b) for $48 \times 25 \times 5$ plates with probes aligned with long axis.

2.1.2 Comparison and repeatability assessment of Conventional and Four-point probe methods

Comparisons between the miniaturised 4 point probe and conventional resistivity measurements were made on samples of grades with binder contents ranging from 6 to 25 %, including two Ni based materials. The samples were provided by a group of hardmetal manufacturers for which a range of properties were assessed, including conventional resistivity measurements from bars; details are given in table 2.1. For some grades, samples were available as both bars $48 \times 5 \times 2$ mm and plates 48×20 (or 25) $\times 5$ mm; for the others only plates were available for testing. 4 point probe measurements were made at the centre of each bar or plate with the probes aligned with longest dimension and correction factors applied from reference 6; conventional measurements were made only on the bars.

Table 2.1 Properties for grades examined in preliminary tests.
Ni binder samples highlighted in bold

Grade – Supplier Code	Binder content (wt.%)	Linear Int. Grain Size (μm)	Magnetic moment $\mu\text{T m}^3 \text{kg}^{-1}$	Hardness (HV30)	Coercivity kA m^{-1}	Resistivity $\text{n}\Omega \text{m}$
x160	10	0.64	1.26	1626	18.5	218
t25	24	0.77	2.82	980	6.8	257
h10	10	0.41	1.49	1367	18.2	205
ma14	14	0.91	1.98	1206	9	177
n15	14.5	0.49	1.75	1248	14.7	215
ma6	6	1.03	0.87	1518	12.3	180
cwn8	8	0.68	0.09	1349	<0.05	237
k322	9.75	0.71	1.26	1374	14.4	228
k3520	20	2.3	2.88	846	5.1	201
k801	6	2.7	0.18	1022	4.3	170

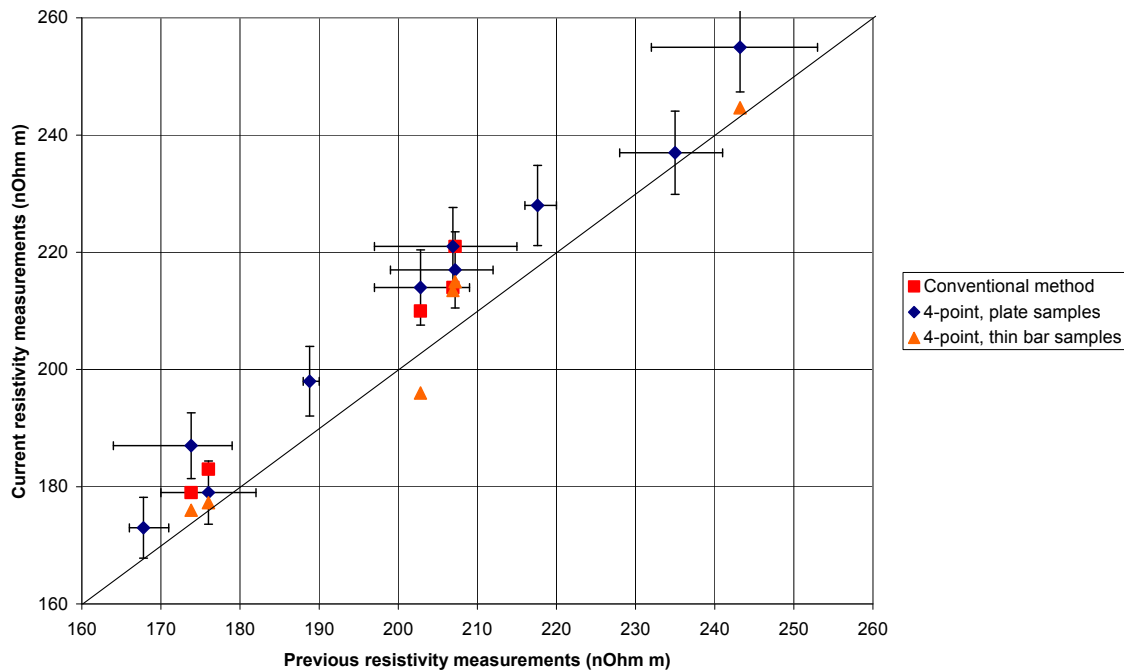


Figure 2.4 Comparison of resistivity measurements by four-point probe and conventional four terminal methods with measurements on samples reported in earlier work.

Figure 2.4 plots resistivity calculated from measurements made by four-point probe, and where possible conventional methods, against preliminary resistivity measurements made using a conventional method in an earlier exercise. Error bars for these earlier resistivity measurements are derived from the range of values measured on 5 different samples. The error bars for the four-point probe are based on ± 2 standard deviations where the standard deviation is calculated from over 20 four-point probe measurements on 4 different samples of the same grade.

The recent measurements made by the different techniques on the same samples agree reasonably closely with each other. There is also a correlation with the earlier measurements, but with an offset from exact agreement of about 5%, even for the same conventional method. The offset for all three methods points to a systematic error in the earlier results, although it is difficult to guess at the possible sources of such an error since a 5% error in the probe separation for the earlier measurements would equate to an error of 0.4 mm for a 8 mm separation, and standard resistors have uncertainties of better than 0.1%.

Resistivities measured by the four-point probe on the thick plates are generally larger than those measured by the same method on thin bars; better overall agreement with previous programme measurements could be obtained if the correction factor used was 0.95 rather than the 0.985 used, but this is significantly larger than that calculated from either reference 5 or reference 6. An error in the correction factor used for the thin bar is much more likely since the factors change much more quickly for small changes in thickness or width. Reversal of the current and averaging of forward and reverse readings should minimise effects of contact resistance. Ohmic heating of the sample could introduce errors, but this effect can be checked for by taking repeated

readings at a constant current and noting if steady readings are obtained or, in the case of heating, a slow drift in readings as the resistance changes.

Other sources of error include the measurement of voltage or current, of which the latter is the most likely since for the four-point method with a 1 mm probe spacing, a current of 1 A will only produce a voltage of 40 μV for a typical hardmetal with a resistivity of approximately 200 $\text{n}\Omega\text{m}$.

2.2 CASE STUDIES

Clearly simple geometries are required if absolute measurements of resistivity are to be made to allow calculation of composition. For the conventional four terminal method long thin bars are needed, or for the miniaturised four-point probe, then thicker (ideally $> 5 \text{ mm}$) and wider (ideally $> 20 \text{ mm}$) samples reduce the significance of the correction factors required.

An alternative approach for use of the four-point probe with more complex geometries (on, for example, thin walls, lack of flat surfaces) would be to establish baseline samples with acceptable compositions having identical complex geometries. If measurements are then made on unknown samples in exactly the same relative position, then the (unknown) correction factor will be constant so that results can be compared directly with the baseline sample. This approach is particularly useful for:

- a) large components which may be too large to fit directly in a coercimeter or a magnetic saturation measurement coil, and
- b) as will be shown below, also for Ni based materials with little or no magnetic moment with a geometry unsuitable for the standard resistivity method.

2.2.1 Co binder phase WC Cylinders

Ten as-sintered “buttons” (solid cylinders approximately 10 mm in length and diameter with rounded ends) from a single batch of WC- 6 wt.% Co were supplied by Marshalls Hard Metals. Carbon contents in the samples were varied by sintering under different conditions, and assessed by measuring coercivity and magnetic saturation for each individual sample at Marshalls. Magnetic saturation was also measured at NPL. Resistivity was measured with the miniaturised four-point probe; because of their small size, and thus the need to ensure a constant geometry for each measurement, the samples were placed in a V-block against an end stop, with the V block held in a fixed position below the four-point probe such that the probes aligned with the cylinder axis. A correction factor was not calculated for this sample geometry, so the “resistivity” recorded was not the true resistivity, but a value increased by a constant (the inverse of the correction factor). At least 3 measurements made at 3 points around the circumference of the sample from which an average uncorrected resistivity was calculated.

Figure 2.5 compares measurements of the magnetic moment of the binder phase by NPL and Marshalls; the NPL measured values were lower by approximately $0.4 \mu\text{Tm}^3\text{kg}^{-1}$ on average, or about 3%, with the scatter range about 1%. This difference is a consequence of the different saturation fields associated with different

test equipment at each organisation. It was noted in the introduction that there can be a close correlation between coercivity and magnetic saturation, and this is seen in Figure 2.6, with a scatter in the repeat measurements made on each sample of about 2%.

Figure 2.7 shows plots of resistivity (uncorrected) against magnetic moment and against coercivity. Resistivity error bars show the total range for the 3 measurements made. Similarly the coercivity error bars reflect the range of measurements while the magnetic moment error bars are estimated as the 1% scatter in figure 2.5. If the single outliers for resistivity for the two mid range samples were excluded, the scatter would be approximately 3%. Some of the general scatter may result from slight variation in size of the as-sintered samples (changing the correction factor), or in some cases slight off-axis alignment in the V-groove.

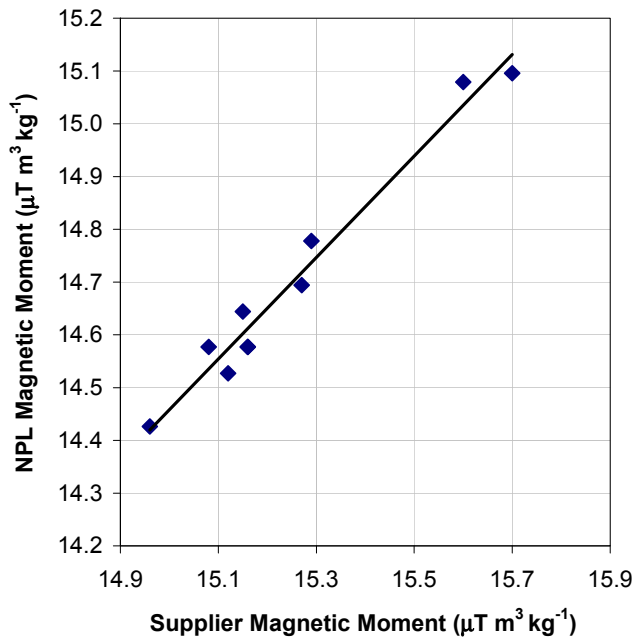


Figure 2.5 Comparison of magnetic moment measurements with two different devices

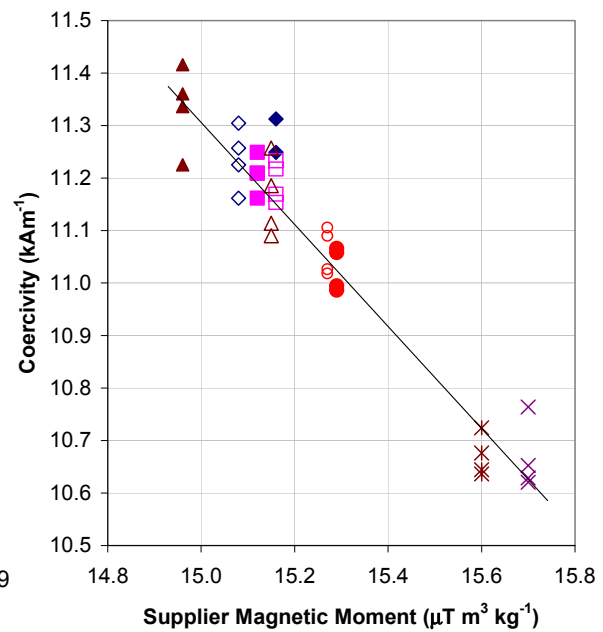


Figure 2.6 Correlation of coercivity with magnetic moment. Each symbol represents a single sample measured 4 times

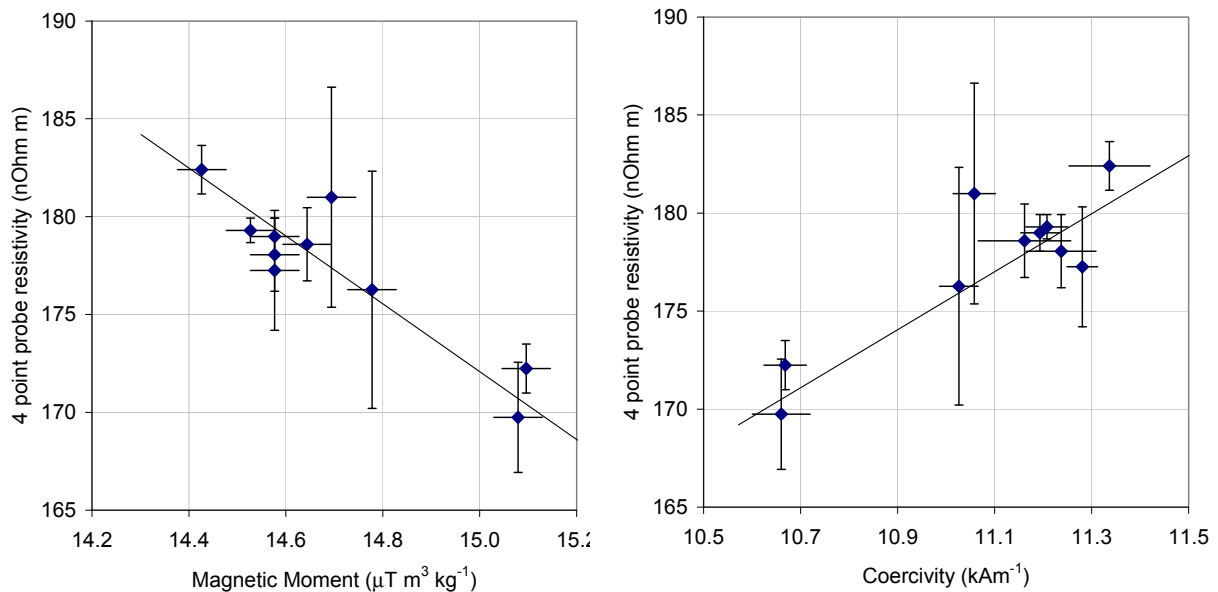


Figure 2.7. Comparison of resistivity measurements with a) magnetic moment and b) coercivity. See text for details of error bars.

2.2.2 Ni binder phase cylinders

Thin walled cylindrical rings of a WC-6 wt% Ni hardmetal were supplied from two batches by Marshalls Hardmetals. With a wall thickness of 1 mm, the rings were cylindrically ground to give a variation of <0.005 mm on the 12 mm outside diameter and surface ground on the ends to 12 ± 0.01 mm lengths. Measurement of magnetic saturation yielded very low or even zero values which made distinction between samples very difficult by this method.

Measurement of magnetic saturation was attempted at NPL, and resistivity was measured in the same way as for the solid Co based cylinders described in the previous section.

Figure 2.8 shows the uncorrected resistivity plotted against the hardmetal magnetic moment. Resistivity values are the average of at least 3 measurements made at 3 points around the circumference of the sample. Magnetic moments could be measured for some samples, but at very low levels (about 0.1% of the values measured for the Co samples), which may account for some of the scatter when plotted against the (uncorrected) resistivity. Despite the scatter there is an indication of increasing resistivity with decreasing magnetic saturation, and significantly, samples for which no magnetic saturation could be measured still showed significant differences in resistivity. This suggests that resistivity measurement can distinguish between samples where there is little or no measurable magnetic saturation.

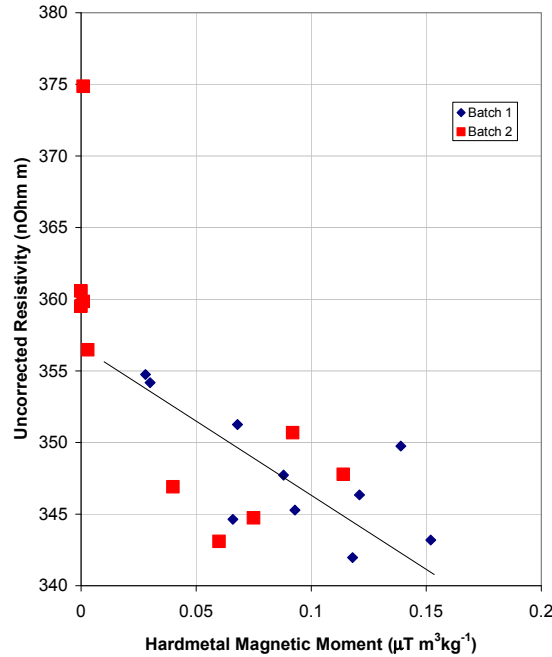


Figure 2.8) Resistivity measurements of parts from two batches of thin walled 6wt% Ni binder hardmetal cylinders.

2.2.3 Ni binder phase bars

A set of 30 25 x 7 x 5 mm bars were produced by Marshalls Hard Metals from a single WC - 10% Ni batch and sub-divided into 6 subsets (numbered 0,3,5,8,9 and 10) which were then presintered under different conditions to achieve a range of solute concentrations of W in the Ni, at the low C end of the two phase field. Magnetic moment and coercivity measurements were made at Marshalls and the former repeated at NPL. Four-point probe resistivity measurements were made with the probes in the centre of each sample and aligned with the long axis of the sample.

Table 2.2 tabulates the magnetic measurements on the samples. For all but two of the subsets no coercivity could be measured at all. Two subsets, 5 and 9, also gave no value of magnetic moment for any of the samples when measured by Marshalls, although the NPL system appeared to be slightly more sensitive at very low magnetic moments, measuring very small values although subset 5 values were all $\leq 0.01 \mu\text{T m}^3\text{kg}^{-1}$. Comparing these NPL magnetic moment measurements with those of resistivity in Figure 2.9 suggests a correlation, but the subsets appear to divide into two groups, with subsets 5 and 9 displaced to lower resistivities compared with the general trend displayed by subsets 0, 3, 8, 10. Discussion of these results and their relationship with microstructure is considered further in section 3.4. There is no obvious connection between the coercivities for subset 8 and the samples in subset 10 with resistivity, but there are very few data points from which to draw conclusions.

Table 2.2 Measurements of magnetic properties of 6 subsets of a WC - 10% Ni hardmetal.

Sub Set	Number	Supplier Coercivity kA m ⁻¹	Supplier Magnetic Moment $\mu\text{Tm}^3\text{kg}^{-1}$	NPL Magnetic Moment $\mu\text{Tm}^3\text{kg}^{-1}$	Sub Set	Number	Supplier Coercivity kA m ⁻¹	Supplier Magnetic Moment $\mu\text{Tm}^3\text{kg}^{-1}$	NPL Magnetic Moment $\mu\text{Tm}^3\text{kg}^{-1}$
0	1	<0.05	2.48	2.47	8	1	20.1	1.33	1.38
0	2	"	2.45	2.48	8	2	23.3	1.38	1.45
0	3	"	2.50	2.52	8	3	20.3	1.45	1.43
0	4	"	2.42	2.52	8	4	22.3	1.45	1.47
0	5	"	2.45	2.48	8	5	<0.05	1.20	1.25
3	1	"	-	0.30	9	1	"	-	0.21
3	2	"	0.33	0.45	9	2	"	-	0.14
3	3	"	-	0.24	9	3	"	-	0.22
3	4	"	-	0.28	9	4	"	-	0.21
3	5	"	0.31	0.42	9	5	"	-	0.21
5	1	"	-	0.02	10	1	15.7	-	0.24
5	2	"	-	0.09	10	2	22.1	0.21	0.36
5	3	"	-	0.08	10	3	<0.05	-	0.24
5	4	"	-	0.06	10	4	"	-	0.30
5	5	"	-	0.12	10	5	"	-	0.21

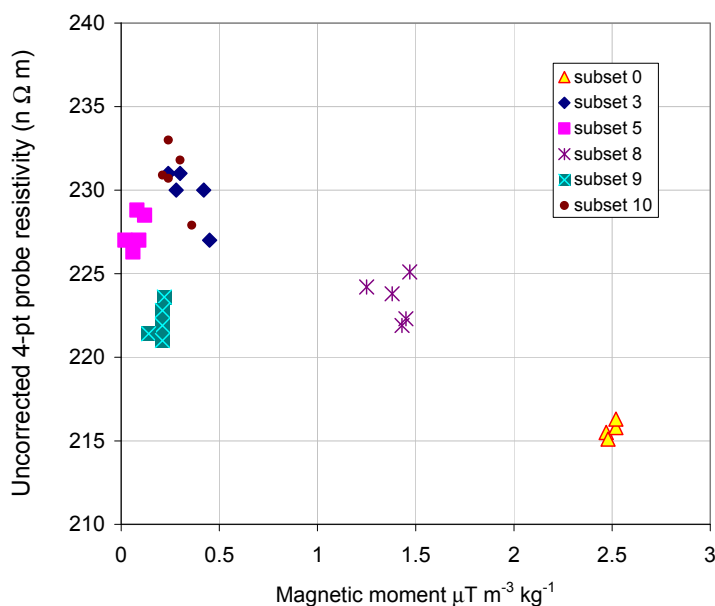


Figure 2.9 Relationship between resistivity and magnetic moment for a 10% Ni binder content hardmetal sintered to give 6 subsets with different carbon content. Note subsets 5 and 9 appear to form a separate cluster of results.

2.3 RELATIONSHIP BETWEEN RESISTIVITY AND MAGNETIC PROPERTIES

Because the magnetic saturation and coercivity both vary in the Co binder phase cylinders of case study 1, indicating a change of both binder phase composition and grain size it is not possible to illustrate the relative effects of these properties on the resistivity. A clearer picture emerges however if the results from the measurements on the wide range of samples described in section 2.1 are plotted against binder content and compared with the variation of magnetic moments measured on the same samples.

The heavy black lines within Figure 2.10 show the maximum and minimum magnetic moment values which define the composition limits within which the binder phase must be controlled to avoid free graphite (above the maximum magnetic moment) or eta phase (below the minimum). It can be seen that, with the exception of the two Ni based materials (ringed), the samples tested fall within these limits for magnetic moment, but are generally close to one or other limit. Those close to the upper free graphite magnetic moment limit have a corresponding low value of resistivity, and conversely those close to the lower eta phase limit have a high resistivity. Unlike the magnetic moment however, there is no significant increase in resistivity with binder phase content. While the change in resistivity must be related to the change in composition of the binder phase, it is not possible to draw clear single limits for all samples for resistivity in the same way since it is thought that grain size has an effect on the resistivity too⁴.

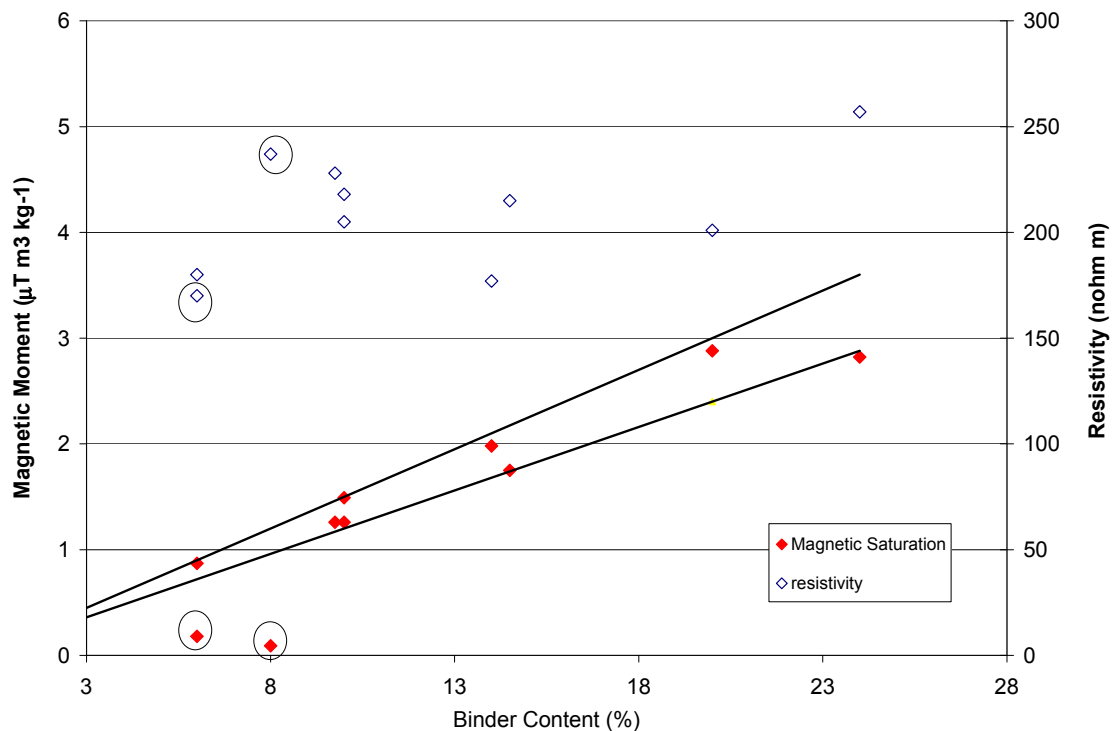


Figure 2.10 Magnetic Moment (left axis) and Resistivity (right axis) plotted against binder content. Ni binder materials ringed. The heavy black lines show the maximum and minimum magnetic moment values which define the composition limits in Co based materials within which the binder phase must be controlled to avoid free graphite (above the maximum magnetic moment) or eta phase (below the minimum).

3 EDDY CURRENT PROBE

The Co and Ni bonded samples described in section 2.3, whose resistivity was measured with the four-point probe were also studied with an eddy current probe. The probe, with associated electronics, was supplied by Micro-epsilon⁸ and would conventionally be used for measuring probe-sample separation from the effect on the coil inductance of varying the air gap between the probe and a standard substrate. The probe is a coil with a single winding of 2 mm diameter, and the electronics could be tuned (normally for a steel substrate) to provide an output of 0 to 10 V for probe-sample separations of 0 to 1 mm. The measurement frequency used was 2 MHz, which for hardmetals, assuming a relative permeability of 50 is estimated to give a skin depth of approximately 25 μm .

In the present case the probe – sample separation was held fixed for the full range of samples, and the effect of the sample material on the coil inductance (again reported simply on a 0-10 V scale) was measured instead. At a fixed separation, a change in either the resistivity or magnetic properties of the sample material should alter the flow of the eddy currents generated in the material, and in turn alter the inductance of the coil.

Measurements were initially made with a separation of approximately 0.1mm, but it was found that the electronics could be tuned to permit a larger gap of up to 0.5 mm and still give a wide output range for the different samples examined. For the plate samples 48 x 20 (or 25) x 5 mm, measurements were made simply at the centre of the large face to avoid edge effects. For other samples, the probe was moved across the sample surface in fixed steps, maintaining the probe-sample separation to within a few micrometres. Samples were demagnetised before analysis.

3.1 EDDY CURRENT PROBE MEASUREMENTS OVER LARGE BINDER CONTENT RANGE

Figure 3.1 plots the probe output against the previously measured binder content, coercivity and magnetic moment for the wide range of binder contents described previously. Figure 3.1c shows a very close correlation between the eddy current probe response and the magnetic moment of the Co based samples, while there was no correlation with resistivity. Thus for the probe measurement conditions used here, variations in resistivity have little effect on the eddy current probe response.

In addition to the two Ni based samples shown in Table 2.1 and Figure 2.10, Figure 3.1c plots measurements (denoted by a square box) for two further 6% Ni based binder grades supplied by Dymet Alloys. These two grades had no measurable magnetic moment but differed in hardness by approximately 5%. These two extra points emphasise that there is a deviation away from linearity of the probe - magnetic moment relationship at very low magnetic moments. It would appear that the eddy current probe responds strongly to the magnetic moment but in the absence of a ferromagnetic response it may still be possible to distinguish between samples.

The probe described above was also connected to an impedance analyser instead of the Micro-epsilon electronics. This enabled the change in the probe coil impedance to

be measured as a function of excitation frequency, rather than the fixed 2 MHz, and also to use much higher frequencies. Figure 3.2a shows the change in the coil impedance as the excitation frequency was increased between from 5 to 15 MHz, for a fixed probe sample displacement. Figure 3.2b shows most clearly the change in peak height and position for different materials, suggesting further work might yield more information if both these parameters were recorded or if different frequencies were investigated more fully; figure 3.2c shows the changes in impedance measured from the curves in figures 3.2a) and b) and compares them with the direct output voltage produced by the Micro-epsilon electronics

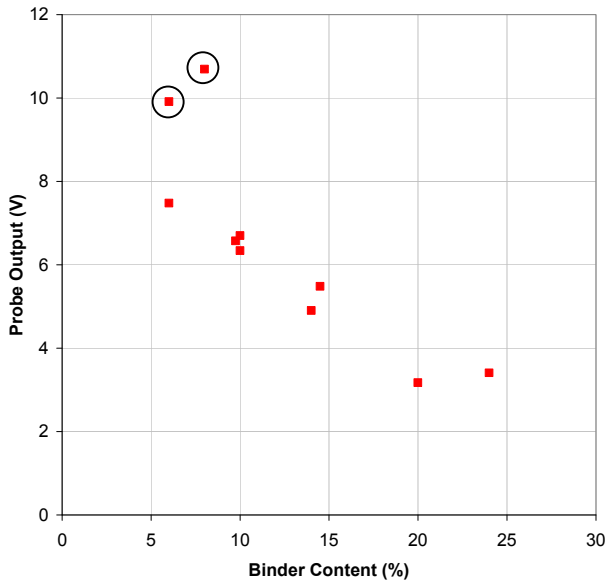


Figure 3.1 a

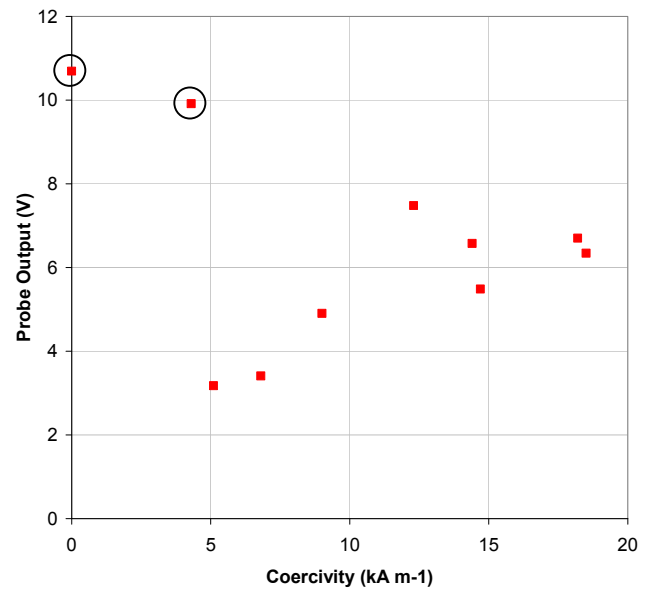


Figure 3.1 b

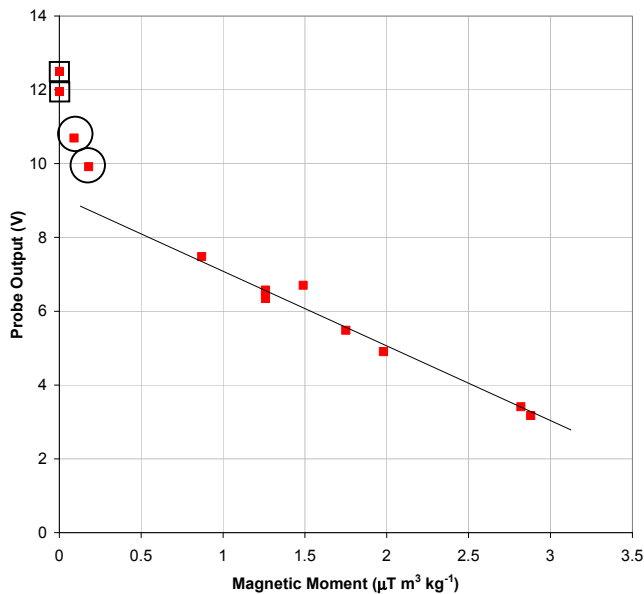


Figure 3.1c

Figure 3.1 Eddy current probe output plotted against a) binder content (Co or Ni, with Ni binder materials ringed), b) coercivity, and c) magnetic saturation. In figure 3.1c) two additional Ni binder materials are plotted, denoted by the square box around the points.

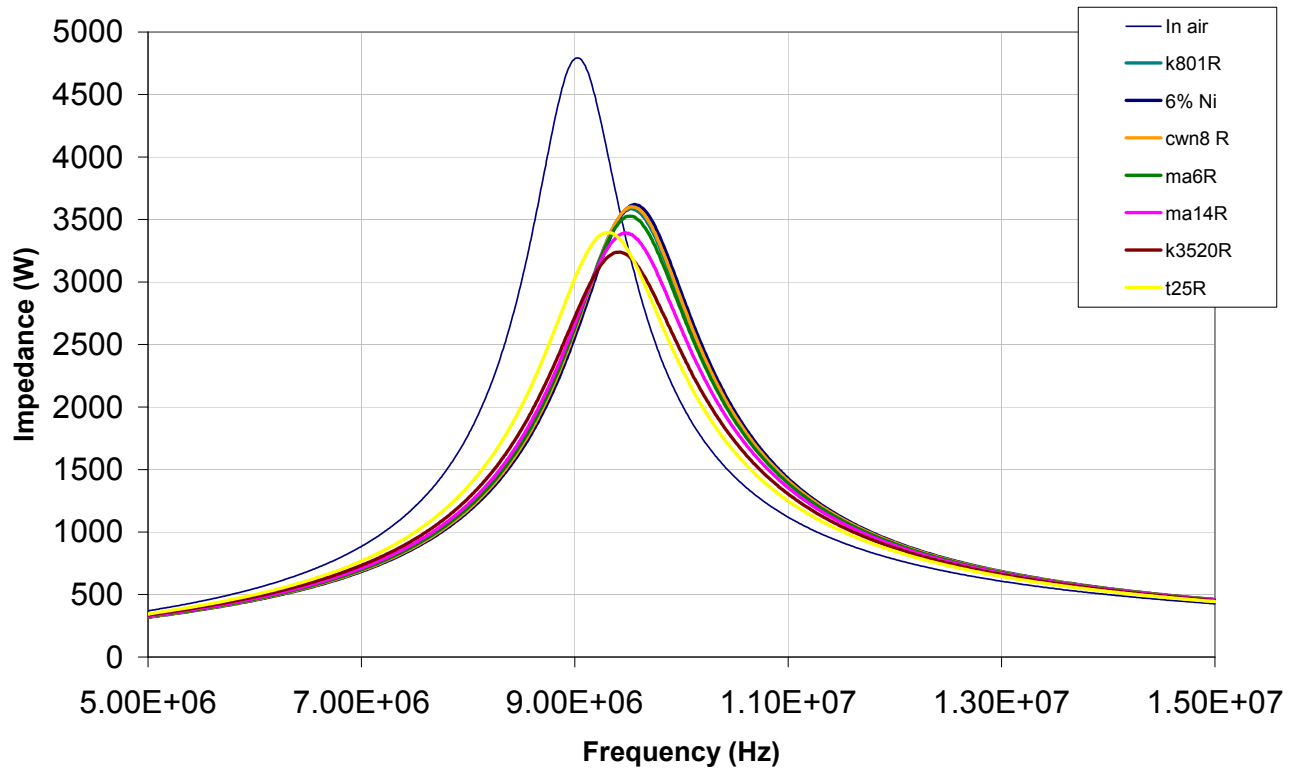


Figure 3.2 a) Probe impedance as a function of frequency ; In air curve produced as a base line when probe positioned at least 10mm from a sample (in practice >1mm sufficient).

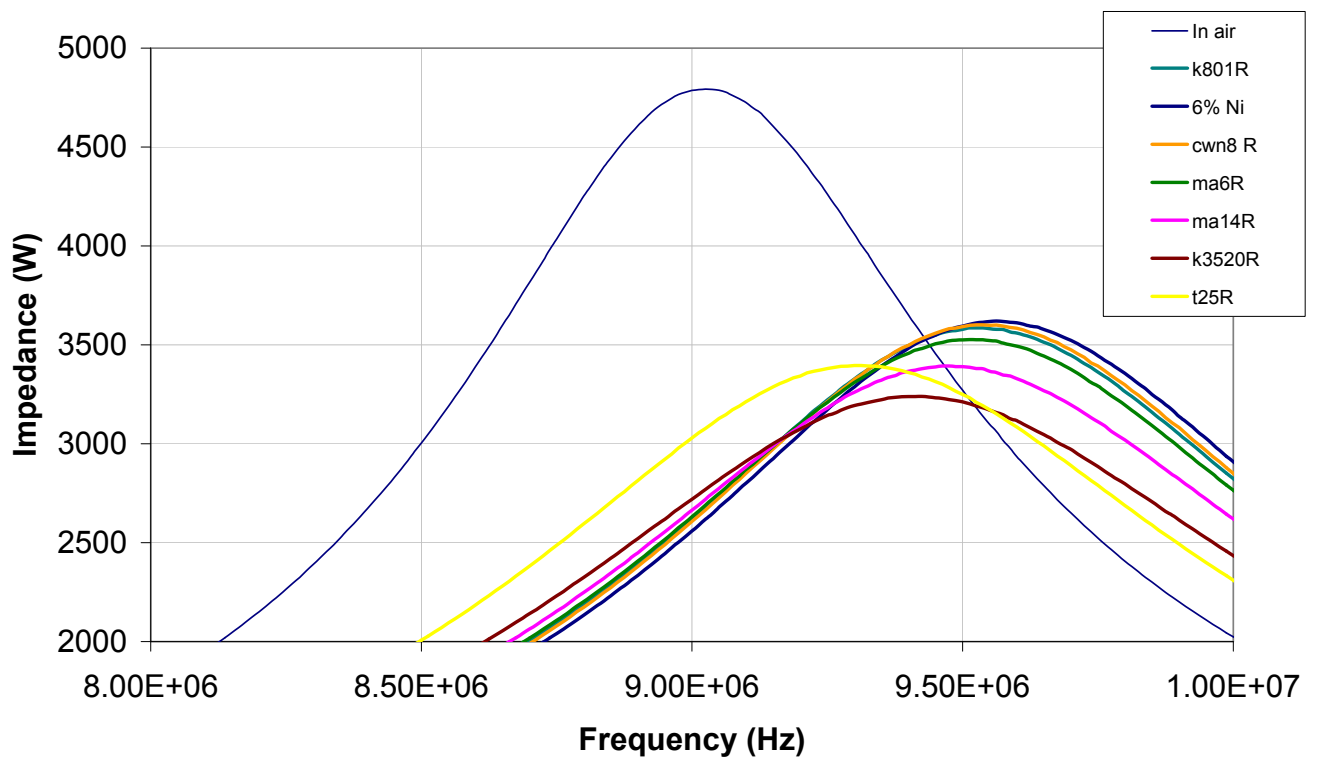


Figure 3.2 b) enlarged section of Figure 3.2 showing detail of resonance peaks

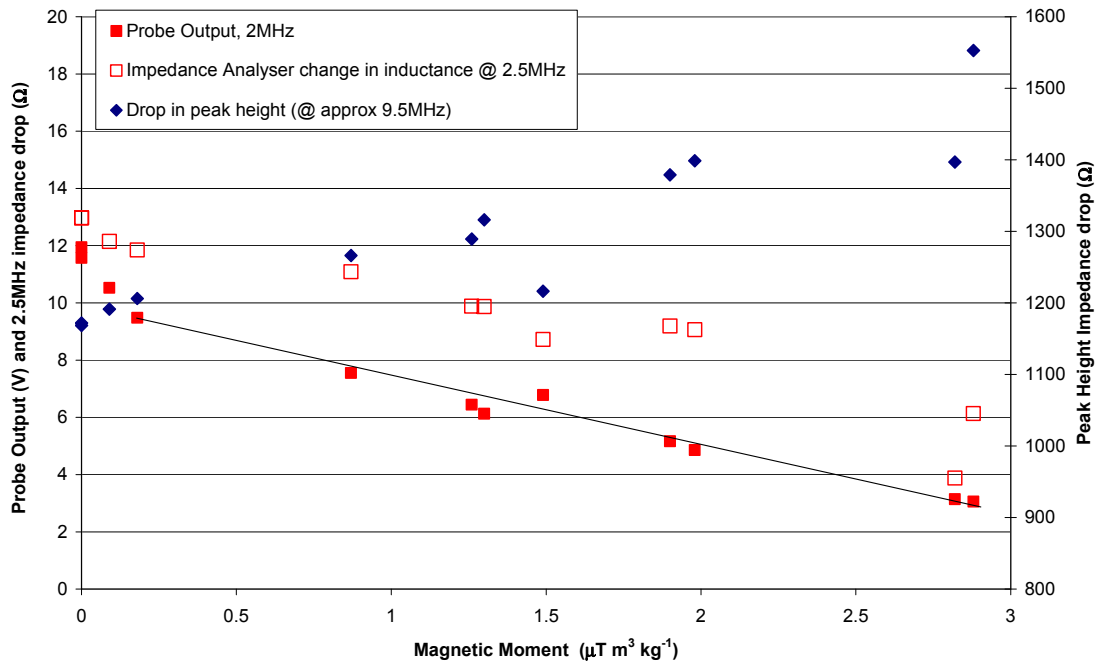


Figure 3.2 c) Comparison with Micro-epsilon probe output values in figure 3.1c) - changes in impedance (from base line in air curve) measured at 2.5 MHz, close to the basic Micro-epsilon 2 MHz, and measured at the peak height of each impedance curve.

3.2 MEASUREMENT OF BINDER PHASE COMPOSITION IN A CO BASED HARDMETAL

The resolution of the eddy current probe (that is, its ability to discriminate between samples) was then examined by testing on samples covering a much narrow range of composition. The samples were all WC - 11% Co bars 5 x 2 x 40 mm produced from the same batch of material but processed to deliberately give a range of W / C solute content in the Co binder.

The bar width of 5 mm was only 2.5 x the size of the probe diameter, so any variation in probe position relative to the edges would significantly alter the probe response. This was minimised by scanning the probe across all the samples, butted together on their long edge, in 0.5 mm steps and recording the probe output at each step (Figure 3.3). Figure 3.4 plots the maximum probe output from each sample (for two measurements made on lines 5 mm apart) against magnetic moment and coercivity measured on the whole sample. The graphs show that the probe has a sensitivity equally as good as, if not better than, the magnetic moment measurement.

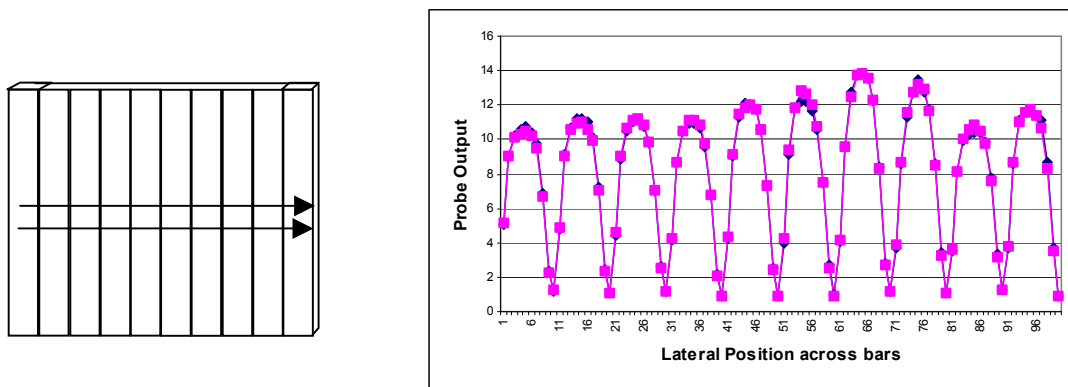


Figure 3.3: Scan of probe across bars. a) Schematic showing bars placed together, with two scanned rows across the bars, 5 mm apart. b) graph of probe output with lateral position across the bars for the two rows of measurements.

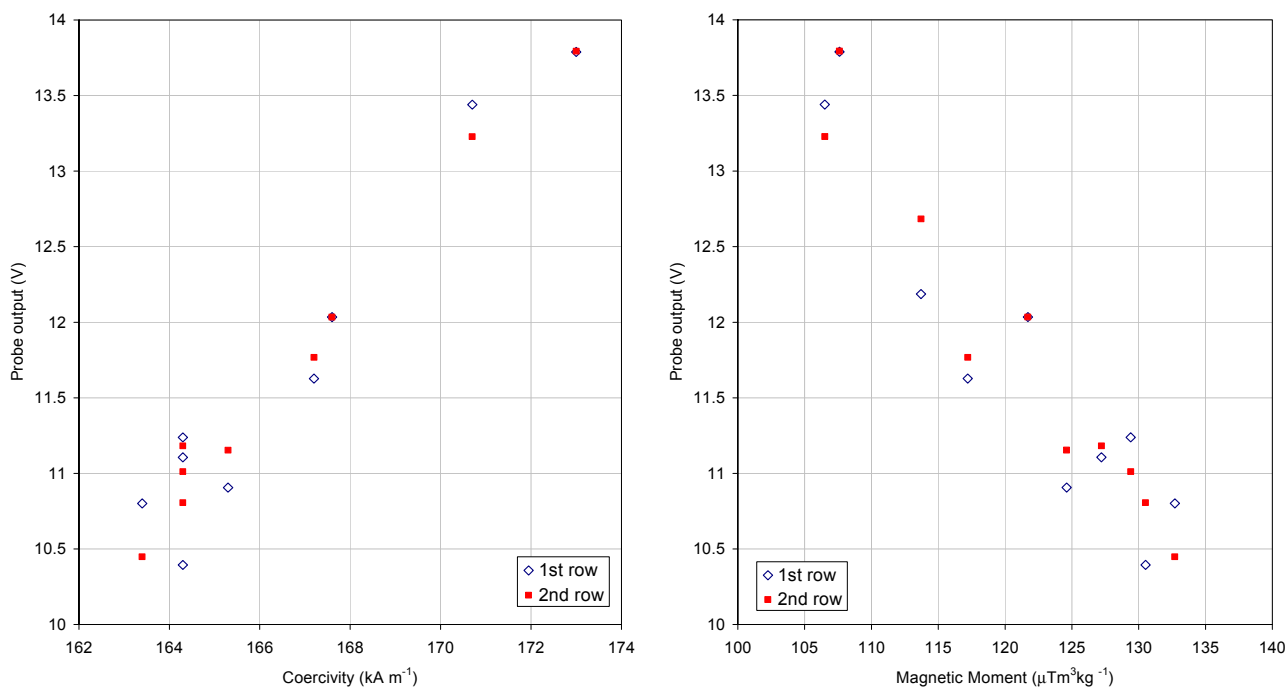


Figure 3.4: Comparison of eddy current probe output with a) coercivity and b) magnetic moment.

3.3 MEASUREMENT OF BINDER PHASE COMPOSITION IN A NI BASED HARDMETAL

In section 2.2.3 resistivity measurements were shown from subsets of a 6% Ni sample with different W and C solute contents. These same samples were evaluated with the eddy current probe, positioning each sample identically below the probe to ensure any edge effects were constant.

Figure 3.5 plots the eddy current output against magnetic moment and against resistivity. Clearly subsets 5 and 9 gave significantly different values from the remaining batches and there appears little discrimination between the remaining subsets. The reasons for this become clear when lift off curves are determined for each sample by recording the eddy current output voltage as the probe-sample air gap is reduced.

The lift off curves in figure 3.6 for the samples of each subset show clearly that subsets 5 and 9 behave very differently from the others and because the measurements in Figure 3.5 were taken at a fixed probe – sample displacement of ≈ 19200 , differences between these samples were clearly resolved, whereas to achieve a similar resolution from the other subsets would require a larger air gap of ≈ 18800 (figures are absolute output values from displacement probe, for which a change of 2000 units is approximately 1mm)

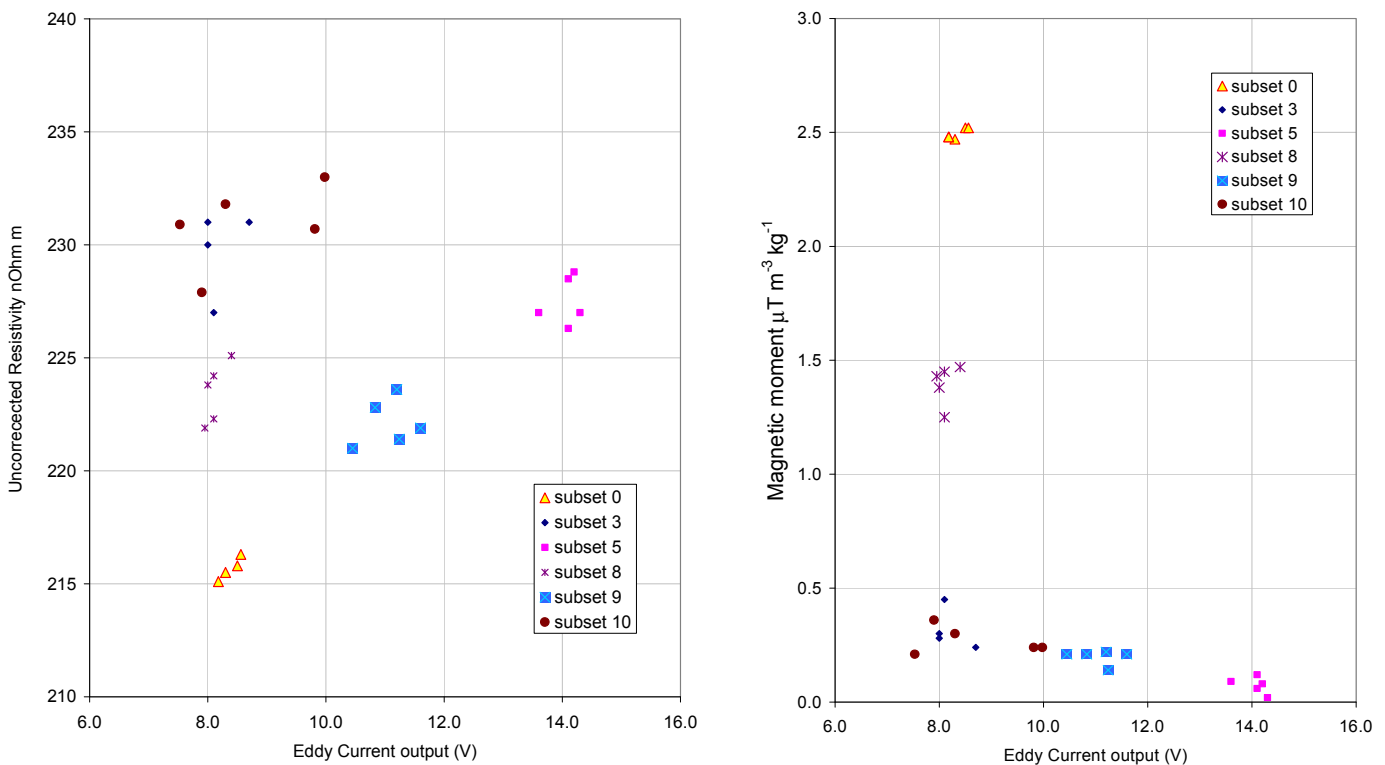


Figure 3.5 Comparison of Eddy current probe output with a) Resistivity and b) magnetic moment for 6% Ni binder samples with different binder solute contents

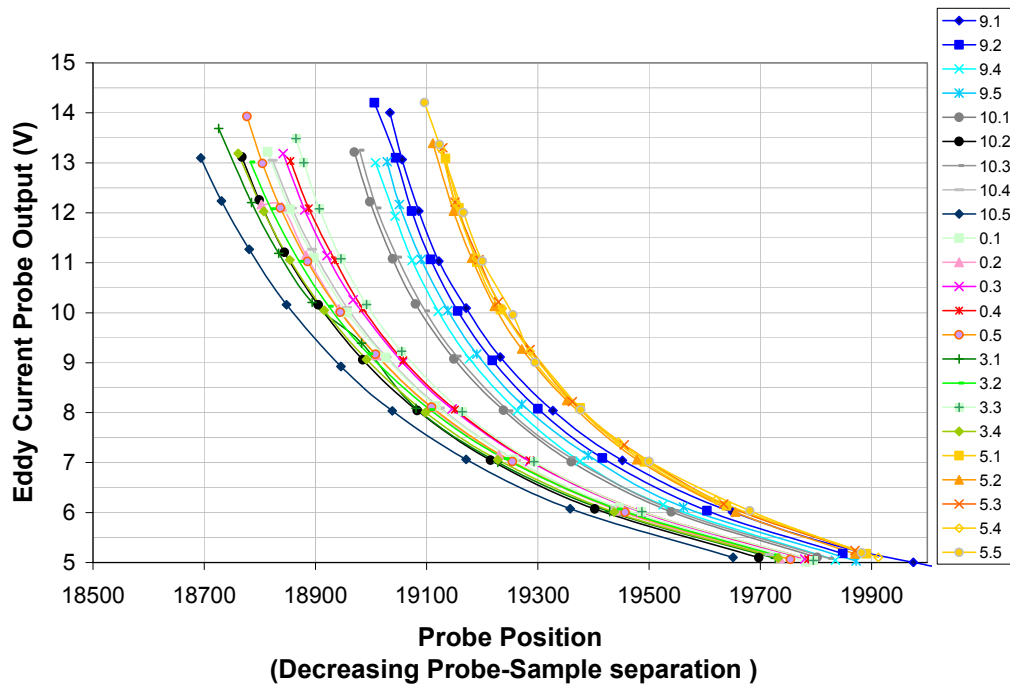


Figure 3.6 Lift off curves for eddy current probe. The y-axis values are the output of the height position encoder, for which an increasing value indicates a decreasing probe-sample separation, and 2000 units $\approx$ 1 mm. At a value of 19900 the probe-sample separation is approximately 0.3 mm. The legend numbers indicate the subset number (0, 3, 5, 8, 9 and 10) first, followed by the sample number (1-5) within the subset.

3.4 RELATIONSHIP OF MAGNETIC MEASUREMENTS TO MICROSTRUCTURE

Figures 3.7 shows secondary electron images of a region from one sample of each of the subsets; little obvious difference can be seen between micrographs. Electron backscatter diffraction (EBSD) maps however reveal a difference in the grain structure of the Ni binder phase, with samples from subset 5 and 9 showing many neighbouring Ni regions between the WC grains to have the same orientation, implying very large Ni grains with sizes much larger than the WC grain size. In contrast the Ni grain size in samples from subsets 0, 3 and 8 and 10 are of the same order as that of the WC. Figure 3.8 shows maps of samples 0, 3 and 9 which illustrate this, and figure 3.9 shows inverse pole figures from all the samples mapped over the same size regions. These clearly illustrate that samples 5 and 9 show only a few principal regions (over the mapped areas, between three and seven regions) with different orientations i.e. large Ni grains. Samples 0, 3, 8 and 10 show many different regions with many different orientations, i.e. small Ni grains. Measurements of WC grain size from these maps (Figure 3.10 and Table 3.1) also show that samples 5 and 9 have a 15% greater WC grain size (circle equivalent diameter) than the other four samples.

It would appear that the different eddy current and resistive measurements measured in subsets 5 and 9 do therefore relate to a different structure of the Ni binder phase.

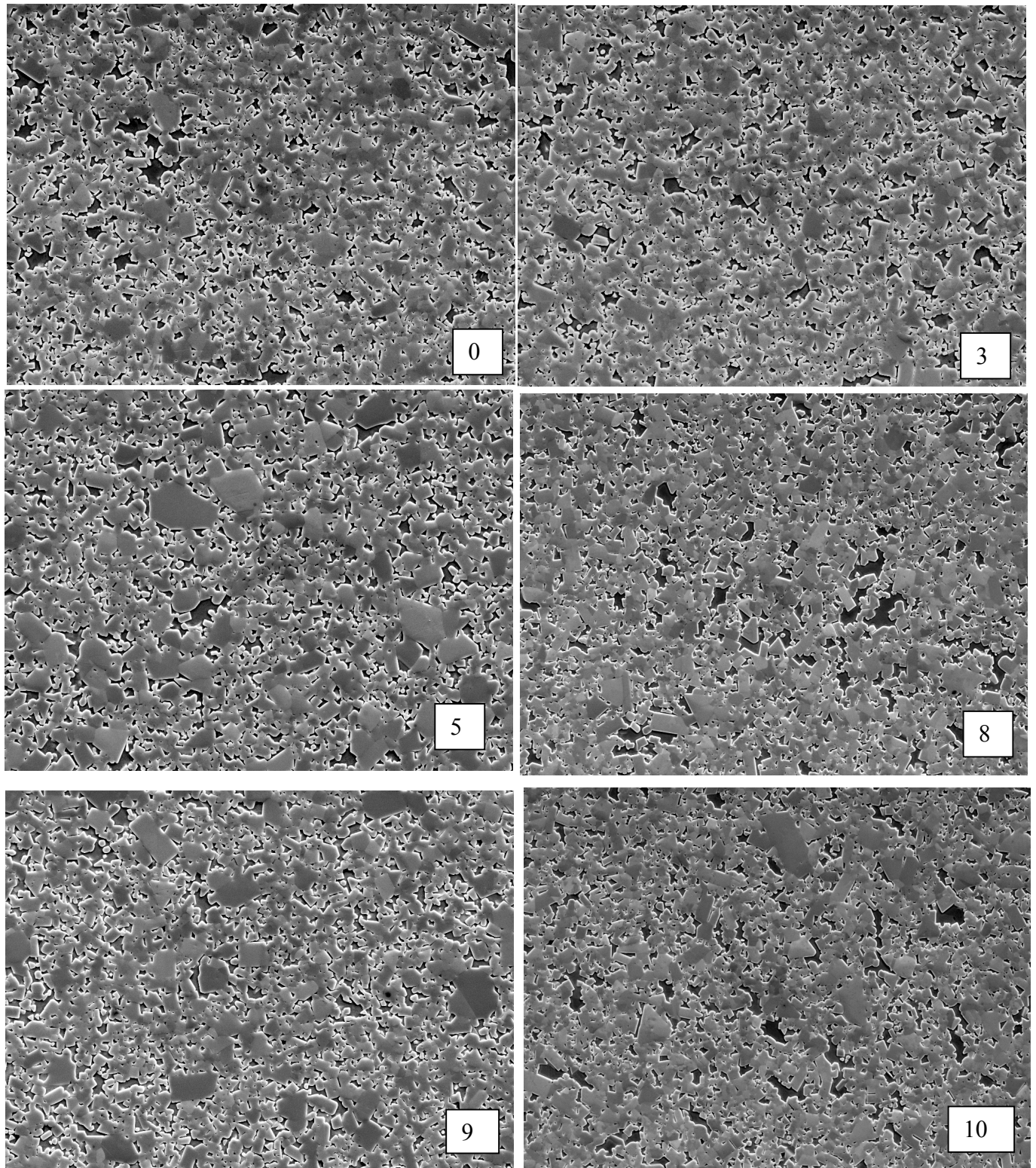


Figure 3.7: Secondary electron images of polished sections of samples from Ni binder subsets with different binder solute contents. Image width = 75 μm in all cases.

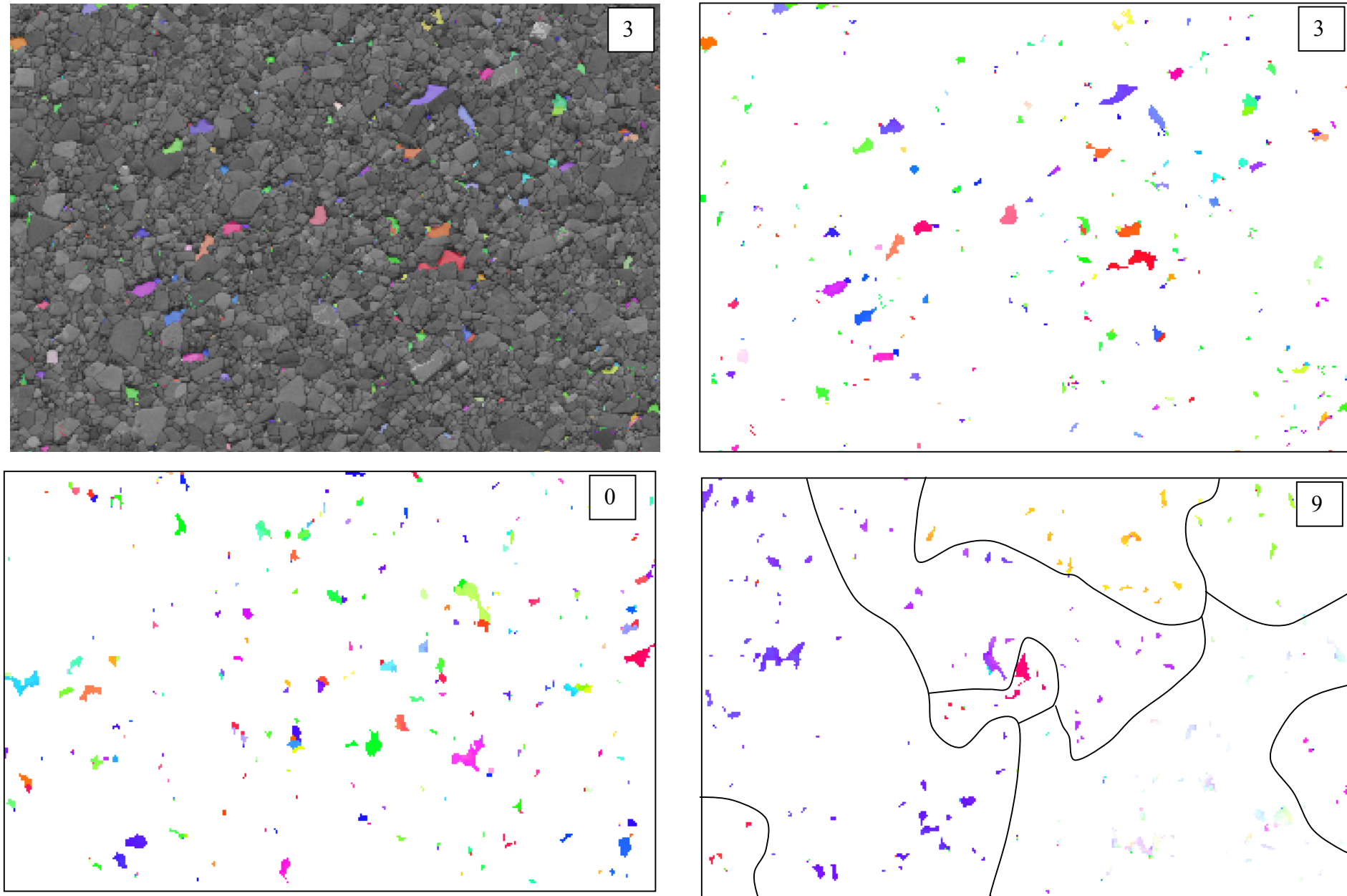


Figure 3.8. EBSD maps of samples 0, 3 and 9. All maps at identical magnifications. Lines on map of sample 9 drawn manually to emphasise areas where the individual Ni regions have a single main orientation.

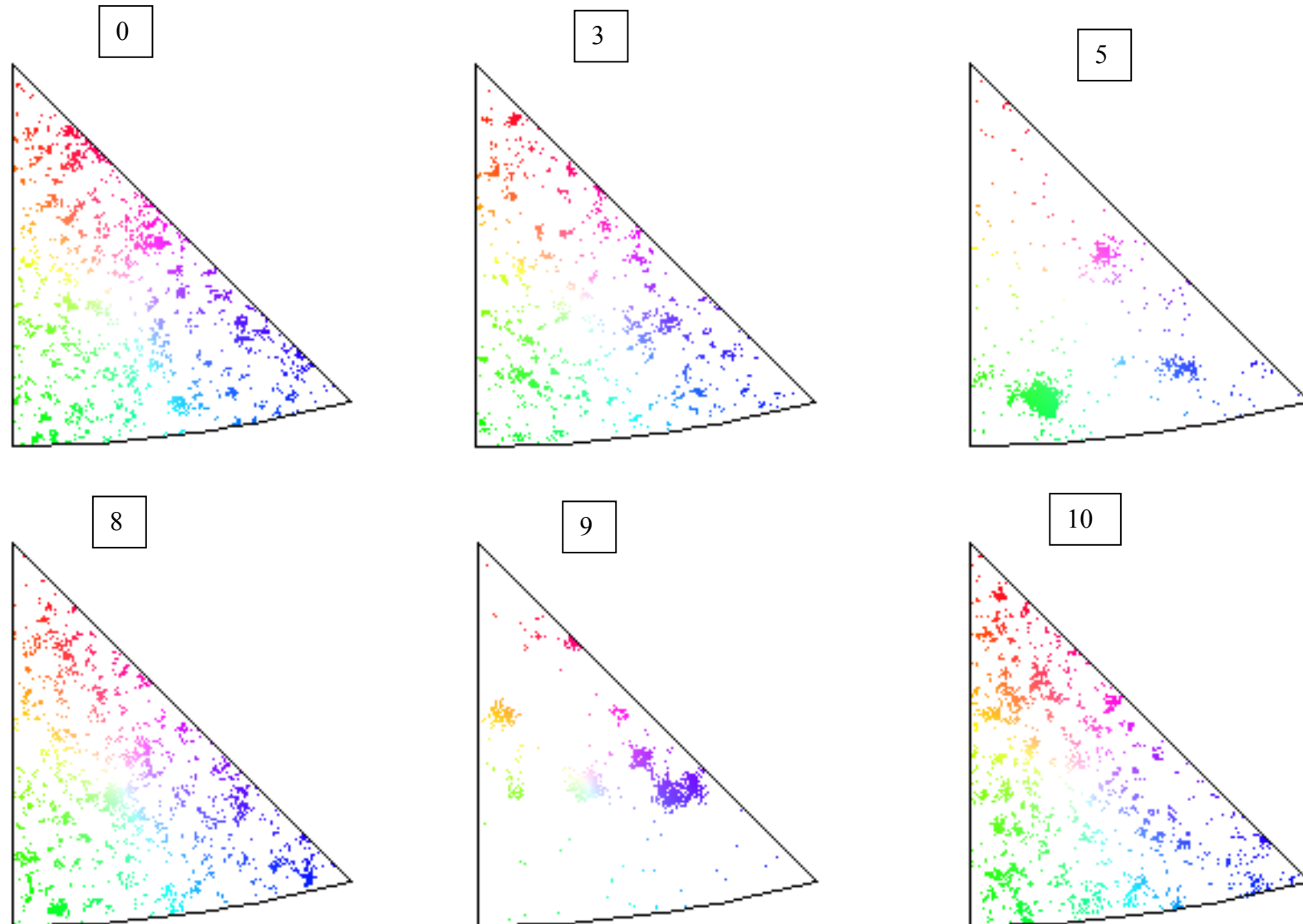


Figure 3.9. Inverse pole figures taken from the maps shown in figure 3.8 and equivalent maps for samples 5,8 and 10

Sample	0	3	5	5rpt	8	9	10
Ni grain size (μm)	0.77	0.80	0.73	0.72	0.74	0.74	0.74
WC grain size (μm)	0.97	0.96	1.12	1.12	0.96	1.21	0.95
Ni no of grains	126	124	137	1171	219	124	250
WC no. of grains.	1145	3403	1833	15939	3400	1908	3499

Table 3.1 Grain size measurements from EBSD maps in figure 3.8 and equivalent maps for other samples. “5rpt” data is from a map of a much larger area of the same sample. Grain size measurements for Ni are for discrete regions seen in maps whether of the same orientation as nearby regions or not.

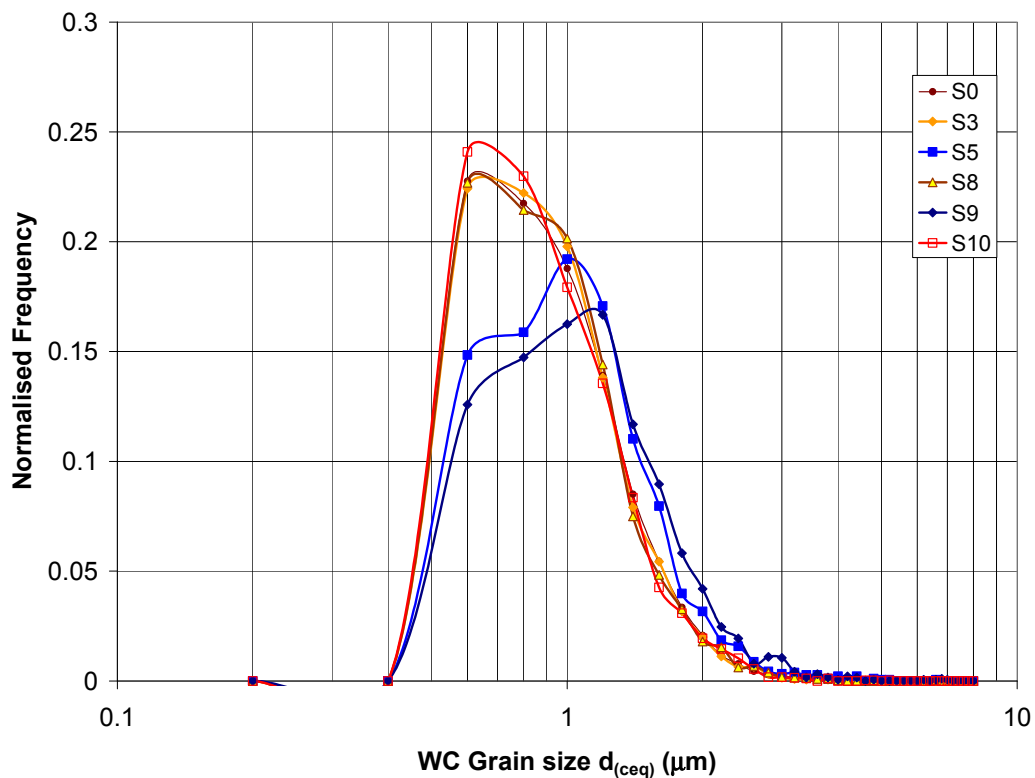


Figure 3.10. WC grain size (circle equivalent diameter) distributions from measurements of grain size on EBSD maps of Ni binder samples 0-10

4.0 SUMMARY

The miniaturised four-point probe can be used to give measurements of resistivity of hardmetal components which do not have a conventional rod or bar geometry. Absolute values can only be obtained by this means from thick samples away from edges, but comparative measurements can be made on any component if the geometry

of the probe and component are kept constant. A reference sample should be used to detect drift in values whether absolute or comparative measurements are being made.

Resistivity has been found to correlate well with coercivity in conventional Co binder hardmetals. In Ni binder hardmetals resistivity would appear to discriminate well between samples produced under different conditions where magnetic measurements are not possible. However it has not yet been established what differences in microstructure are being discriminated by these measurements.

As an alternative to the four-point probe, a small eddy current probe has been shown to be capable of measuring differences between hardmetal samples, with very good correlation between the probe inductance and magnetic moment for Co binder hardmetals. With Ni binder materials the eddy current probe output gives information which is complementary to resistivity data and appears to distinguish between materials with different binder phase grain size and WC grain size, but further work is needed on more samples to understand these measurements fully.

Acknowledgements

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