Resistivity of Hardmetals

EPMA European Hard Materials Group EHMG
Collaborative Research Proposal – October 2012

Proposal

The proposed project will measure electrical resistivity and thermal property data for a wide range of hardmetals between room temperature and 800 ºC, in order to:

- investigate the potential for a new quality control technique with the added advantage of characterising non-magnetic materials and with application to a wide range of sample sizes
- provide data for modelling performance applications where higher temperatures than ambient are experienced

The proposed work can be summarised in the following three objectives:

Objective 1

To investigate the relevance of the Wiedemann-Franz relation for hardmetals (where for pure metals there is a proportionality constant between electrical resistivity and thermal conductivity) by measuring the temperature dependence of resistivity on a range of hardmetals and studying the relation between thermal conductivity and resistivity. Thermal conductivity data to be obtained using laser flash diffusivity experiments or supplied by project partners.

Deliverable: Report on the variation of electrical resistivity and thermal conductivity as a function of temperature for a range of hardmetals and the relationships of these properties to microstructure.

Objective 2

To evaluate the repeatability and reproducibility of various test methods suitable for measurement of electrical resistivity of hardmetal components and to produce recommendations for the specification of a suitable test system.

Deliverable: Report with recommendations for the measurement of electrical resistivity of hardmetals.

Objective 3

To produce a model of the thermal conductivity and electrical resistivity of hardmetals in 3D using a mean field approach

Deliverable: Report on results of modelling thermal conductivity and electrical resistivity with varying parameters for simulated hardmetal microstructures

The two practical objectives would be pursued using materials supplied from the Modulus project, though an additional option might also be to make resistivity measurements on materials with non-magnetic or Ni or Fe-based binder phases.

Rationale and Introduction

Resistivity measurements for hardmetals have the potential for a new quality control technique with the added advantage of being able to characterise non-magnetic materials. It is likely that it will have application to a range of sample sizes. Resistivity has been found to correlate well with coercivity in conventional Co binder hardmetals [1]. In Ni binder hardmetals resistivity would appear to discriminate well between samples produced under different conditions where magnetic measurements are not possible [2]. Roebuck and van den Berg [1] summarised the effects of microstructural 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.

Thermal property data on well characterised materials is needed by industry for optimising the performance of hardmetal components in many applications where heat is generated through contact mechanics. Such data will also contribute for modelling performance applications where higher temperatures than ambient are experienced. Thermal property measurements are not straightforward. Thermal conductivity (k) is generally calculated from thermal diffusivity (α) measurements using the expression

$$\alpha = \frac{k}{D\, C_p} \qquad (1)$$

where D is the density (kg m^{-3}) and C_p is the specific heat capacity (J kg^{-1} K^{-1}). The units of α and k are m^2 s^{-1} and W m^{-1} K^{-1} respectively. Thermal diffusivity measurements are usually conducted using laser flash apparatus [3-6]. Test samples are typically small discs (about 12 mm diameter and 2 mm thick) and measurements are performed at different temperatures in an appropriate vacuum system. Electricity resistivity measurements have the potential for providing information on thermal conductivity through the empirical Wiedemann-Franz (W-F) relation:

$$k\rho = LT \qquad (2)$$

where ρ is the electricity resistivity (Ωm) , T is temperature (K) and L is the Lorenz number (2.44×10^{-8} WΩ K^{-2} for pure metals). This alternative method would be much cheaper and more direct than using laser flash apparatus. The W-F relation holds reasonably well for pure metals; but, hardmetals are two phase and thus accurate experimental measurements are needed to investigate the utility of the W-F relation for these types of material. Table 1 provides some calculated representative values for 6 and 10wt% Co materials.

Table 1 – Approximate room temperature (RT) values

Material+	Density kg m^{-3}	C_p ++ J kg^{-1} K^{-1}	Electricity resistivity nΩm	Thermal conductivity, Wm^{-1} K^{-1}		Thermal diffusivity* m^2 s^{-1}
				Handbook++	W-F*	
WC-6wt% Co	14.9	205	180	95	40	0.031
WC-10wt% Co	14.4	220	210	90	35	0.028

+ Medium grained materials.

* Calculated using the value of L for pure metals. The discrepancy with the handbook value implies a different value of L is needed for hardmetals.

++KJA Brookes World Directory and Handbook of Hardmetals and Hard Materials 6th Edition [7].

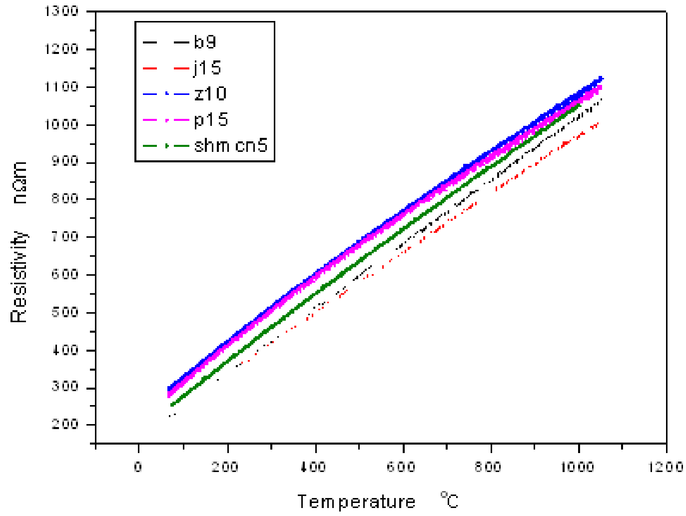

Figure 1 Typical data for temperature dependence of resistivity of hardmetals

A systematic study of the effects of microstructural variables should yield understanding that could be directly applicable to more accurate modelling of the thermomechanical behaviour of hardmetal components. Furthermore, the measurement of these properties will provide an additional tool to quantify the quality of production batches of material since the resistivity will also be sensitive to changes in chemistry and impurity content.

This study would be assisted by the development of a model for thermal conductivity from the known properties of the individual constituents using mean field approaches (MFA) [8-10]. By assuming that the thermal properties are not affected by the fabrication processes, the effect of phase size and shape (and if necessary, orientation) and interfacial properties on the overall behaviour of the material could be modelled to give the theoretical maximum possible conductivities. Validation of the model with experimental measurements would then enable a wider range of structures/compositions to be examined.

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 1.5× 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. Reversing the current allows an average to be determined and removal of the effects of thermal emfs caused by junctions of dissimilar metals. 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. The dependency of the magnitude of uncertainties on testpiece dimensions will be studied. A fully operating system will be described in a report to participating companies.

Typical testpieces for measurements of the temperature dependence of electrical resistivity need to have this preferred shape:

Rectangular Bar - 40 mm long, 2 mm wide, 1 mm thick

It is essential that the dimensions are accurate to ± 0.01 mm and that surfaces are parallel to ± 0.02 mm. These samples could be machined from the materials supplied for the modulus project. Other rectangular, round or disc geometries would be suitable for RT dc resistivity measurements.

References

1 Roebuck, B, and van den Berg, L. Electrical resistivity measurements on WC/Co hardmetals. PM Science and Technology Briefs, 1(3), 1999, 9-13.

2 Mingard, K. and Roebuck, B. Electrical and magnetic measurements of hardmetals with Ni binder phase. NPL Report MAT 33, September 2009.

3 Cowan, R.D. Pulse method of measuring thermal diffusivity at high temperature. J. Appl. Phys., 34(4), 1963, 926-7.

4 Cape, J.A., Lehman, G.W., Temperature and finite pulse-time effects in the flash method for measuring thermal diffusivity, J. Appl. Phys., 34(7), 1963, 1909-1913.

5 ASTME1461-11 Standard test method for thermal diffusivity by the flash method.

6 Parker, W.J., Jenkins, R.J., Bulter, C.P. and Abbott, G.L. Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity. J. Appl. Phys., 32, 1961, 1679-84.

7 Brookes, K.J.A. World Directory and Handbook of Hardmetals and Hard Materials, Int. Carbide Data, East Barnet, Herts, UK, 6th edition, 1996.

8 Eshelby JD. The determination of the elastic field of an ellipsoidal inclusion and related problems. Proc. Roy. Soc. A 241, 376-396, 1957.

9 Mori T, Tanaka K. Average stress in matrix and average elastic energy of materials with misfitting inclusions. Acta Materialia 21, 571–574, 1973.

10 Benveniste Y. A new approach to the application of Mori-Tanaka's theory in composite materials. Mechanics of Materials 6, 147–157, 1987.

Proposed Project Management

The EPMA will oversee the project and ensure that NPL and partners meet their commitments. The EPMA will use various methods (web, etc) to ensure satisfactory dissemination of the project outcomes.

Proposed Project Costs

A working target, including some final testpiece shaping at NPL, would be:

- €69.66k for the thermal and electrical resistivity study at NPL and €3k for complementary thermal diffusivity measurements at CEIT.
- €25.34k for the development of guidelines for a suitable resistivity measurement system
- €15k for the modelling at CEIT.
- €6K for administrative costs of the EPMA

(Total : €119k)

The cost to each participating industrial partner would be dependent on numbers taking part but 50% of the research at NPL will be **co-funded by other NPL projects, reducing their costs to €47.5k**.

So the overall cost of the project to the project partners would be <u>€71.5k</u> (excluding VAT if applicable*).

Costs would be **<u>shared equally</u>** between the industrial participants.

Payment would be made in several instalments. For example six partners would be required to contribute in two instalments a total of ca. €12k each.

** Non UK participants do not pay VAT provided they give their VAT number to the EPMA. UK participants have to pay VAT regardless and then reclaim it.*

The industrial participants will be responsible for the Selection and Manufacture of Test Specimens (WP0).

<u>If you are interested in the project please sign and return to the EPMA the following Consortium Agreement.</u>
<u>If you are not an EPMA member or would like more information please contact Dr Olivier Coube, EPMA Technical Director, oc@epma.com</u>

EPMA European Hard Materials Group
Resistivity of Hardmetals Project
Consortium Agreement
Issued October 2012

The Project - As defined in Annex 1
The Contractors – Materials Division NPL, Materials Department CEIT
The Members - **paid up corporate EPMA members*** funding the Project
The Participants – The Contractors and the Members

UV = unanimous vote; MV = majority vote of 2/3 members or higher
Project Fee = full fee paid at start of Project Stage 1

Heads

1. The Members and Contractors agree to cooperate in order to complete the Project according to Annex 1.

2. All data generated under the Project will remain confidential to the Members during the Project and for THREE years after delivery of the final written report to Members, and may only be disclosed to third parties (e.g. for dissemination purpose in PM Congress) with UV of the Members.

3. The Contractors agree to not carry out a similar project on hardmetals with organisations other than the Members until the completion of the project (delivery of the final report).

4. The Members agree to share equally the cost of the Project (EUR 71,500) through a Project Fee of maximum **EUR 17,875** per Member, excluding the Work Package 0 (Selection and Manufacture of Test Specimens). The required minimum number of Members is **four** unless the Members agree to exceed the maximum Project Fee.

5. The Members also undertake to provide the Contractors with the necessary test specimens and their appropriate surface preparations (Work Package 0 “WP 0”). If no agreement on in-kind contribution between the industrial partners can be found, the EPMA will coordinate the WP 0 and charge equally each Member to cover the cost of WP0 plus an administrative fee of 10%.

6. Payment of fees must be made promptly on receipt of invoice by TT to the nominated EPMA account.

    - 50% at the start of the project
    - 50% after completion of the project stage and delivery of the Final report.

7. New paying members may be admitted during the Project by UV on payment of full Project Fee plus a reasonable premium (10%). No Participation and access to the Project’s results and deliverables is possible after the completion of the project.

8. Each Participant will retain the Intellectual Property for any other outcomes of the project. The Intellectual Property from the Resistivity of Hardmetals reports shall be owned by the Members.

9. The contractor's warranty extends solely to the use of due scientific diligence and to compliance with accepted engineering practice. The contractors do not guarantee that the desired objectives of the research and development project will be achieved.

10. Liability. Each Party is liable solely for wilful actions and gross negligence. Liability for proven damage is limited to the amount of the contractual sum.

11. Coordination will be by the EPMA, who will have responsibility for invoicing, day to day liaison with the Contractors and keeping Members informed. The EPMA will operate under the same confidentiality agreement as Members and the EPMA President will be arbitrator for unresolved disputes by the Members. Should the Parties fail to do so, then such dispute shall be subject to the exclusive jurisdiction of the English Courts. The laws of England and Wales govern all matters arising out of or relating to this agreement, and all transactions contemplated hereby, including, without limitation, its validity, interpretation, construction, performance and enforcement.

12. Except for the terms 4, 6, 7, 9, 10, 11 and 12 all the terms of this agreement may be changed by UV of the Members.

Signatures: signed individually by all Members and Contractors

ORGANISATION:

VAT Number:

NAME:

(Date signed)

***If you are not an EPMA member please contact Dr Olivier Coube, EPMA Technical Director, oc@epma.com**

Annex 1: Work Packages in the Project:
Resistivity of Hardmetals

1. WP 0 Selection and Manufacture of Test Specimens

Programme: Industrial partners to agree suitable testpieces of a range of hardmetals with varying Co content (5-30 wt%), WC grain size (0.5-5 μm) and carbon content (across the two phase WC-Co region). Ni binder materials could also be provided for testing. This would be a significant in-kind contribution to the project. Materials from the modulus project are probably suitable, but others could be supplied by negotiation.

Distribution of tasks:
- Selection of materials : **all partners.**
- Supply of material data: **Industrial Partners**
- Surface preparation: industrial partners to supply specimens ground to shape and blanks for common grinding route at NPL. **Industrial Partners**
- Measurement/supply of static properties: **Industrial Partners**
- Pre-test (if necessary) and final test samples shaping: **NPL**

Cost:
- Contribution by Members (industrial partners): cost not included here. If no agreement on in-kind contribution between the industrial partners can be found, the EPMA will coordinate the WP 0 and charge equally each Member to cover the cost of WP0 plus an administrative fee of 10%.

Estimated duration: Months1-6. **Deliverables**: Test samples (see presentation of the project)

2. WP 1 Measurement of Temperature Dependence of Electricity Resistivity

Programme: NPL will measure the temperature dependence of electricity resistivity. Thermal diffusivity of these materials would be measured at NPL, with an additional 10 samples at CEIT to investigate the measurement repeatability, and the thermal conductivity calculated from the diffusivity would be compared with resistivity to verify if or how the W-F relation is followed. The data would also be compared with results of modelling in WP3. If the Modulus project materials are used then the microstructures have already been characterised: WC grain size has been measured using EBSD and Co composition has been ascertained using magnetic moment values. Further samples will be polished for grain size determination. A final NPL report for partners would be prepared.

Distribution of tasks: NPL, CEIT:
- Resistivity – Temperature Measurement (Existing Samples and Alternative Materials)
- Thermal Diffusivity Measurement (at NPL with an additional 10 Samples at CEIT)
- Microstructural Measurement

Estimated duration: Months 1-18. **Deliverable**: Report on the variation of electrical resistivity and thermal conductivity as a function of temperature for a range of hardmetals and the relationships of these properties to microstructure.

3. **WP 2 Review of Hardware and Software Resistivity Measurement**

Programme: NPL would review the hardware and PC software available and assess conventional and miniature dc resistivity measurements to provide participating companies with the information to acquire suitable test rig and instrumentation themselves for making measurements on their own materials.

Distribution of tasks: NPL:
- Resistivity R and R Study
- Evaluation of Size Limitations
- Report

Estimated duration: Months 7-18. **Deliverables**: Report with recommendations for the measurement of electrical resistivity of hardmetals.

4. **WP 3 Modelling and Numerical Simulation**

Programme: CEIT will predict the thermal conductivity of hardmetals from the known properties of the individual constituents using mean field approaches (MFA). The goal is to obtain the theoretical maximum possible conductivities assuming that the thermal properties are not affected by the fabrication processes and to study the effect of phase size and shape, (orientation, if necessary) and interfacial properties on the overall behaviour of the material. The study will be extended to electrical conductivity but in this case the extension of MFA in the form of the differential effective medium approach (DEM) will be evaluated as it is known that the predictive differences between both techniques for composite materials behaviour increase with high volume fraction and very high phase contrast.

Distribution of tasks: CEIT:
- Development of model
- Validation by comparison with experimental results
- Effect of microstructure and interfacial properties on thermal conductivity and resistivity

Estimated duration: Months 7-12. **Deliverables:** Report on results of modelling thermal conductivity and electrical resistivity with varying parameters for simulated hardmetal microstructures

5. **WP 4 Project Management and Reporting**

Programme: The EPMA will oversee the project and ensure that NPL and partners meet their commitments. The EPMA will use various methods (web, etc) to ensure satisfactory dissemination of the project outcomes.

Distribution of tasks:
- Project Management: **EPMA**
- Final Report: **EPMA , NPL, CEIT**

Estimated duration: WP 0-3 + 1 Month for Report

6. Costs:

NPL: €47.5k, (WP 1 and WP 2); CEIT €18k (WP1 and WP3); **EPMA**: ca. 10% Administrative cost of WP 0-3 (WP4 + Travels): €6k
Total Cost: WP1-4 = € 71.5k (excluding VAT if applicable and WP 0)
Estimated total duration: ca. 18 Months

7. Proposed Project Timetable:

It is anticipated that practical work in the project would commence at the start of 2013 and be completed within 18 months. Three meetings with all contractors would be held, a kick-off meeting, one approximately half way through to report on progress and one wind-up meeting at project completion. Work at partner organisations to prepare materials should start as soon as the project has sufficient members to meet the financial requirements.

	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J
Kick-off meeting/Agreement of Programme	■																	
Selection of sample compositions	■																	
Manufacture of new samples	■	■	■	■	■	■												
Reporting Meeting										■								
Final Meeting																		■
WP1																		
Existing Samples																		
Resistivity - Temperature measurement	■	■	■	■	■													
Thermal Diffusivity	■	■	■	■	■	■	■	■	■									
Alternative Binder Materials																		
Resistivity - Temperature measurement							■	■	■	■	■	■						
Thermal Diffusivity							■	■	■	■	■	■	■	■	■	■		
Microstructural Measurement							■	■	■	■								
Final report																	■	■
WP2																		
Resistivity R and R study							■	■	■	■	■	■						
Evaluation of Size limitations									■	■	■	■	■	■				
Good Practice Guide													■	■	■	■	■	■
WP3																		
Development of model						■	■	■	■									
Validation by comparison with experimental								■	■	■								
Effect of microstructure/interfaces										■	■	■						