ESRF	**Experiment title:** The characterisation of Zn-recycled cemented carbide cutting tool through multiple recycling lifetimes using XRF nanoprobe	**Experiment number**: MA-3505
Beamline: ID16B	**Date of experiment**: from: 15 May 2017 to: 19 May 2017	**Date of report**: 10 September 2017
Shifts: 9	**Local contact(s)**: Dr.Vanessa Isabel Tardillo Saurez	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Prof. Carlos Alfredo Pineda Vargas*[1]

Dr. Christopher Freemantle*[2]

Dr. Miroslava Topic[1]

Dr. Gema Martinez Criado*[3]

1) Ithemba Laboratories, Somerset West, South Africa
2) Pilot Tools, Johannesburg, South Africa
3) Spanish National Research Council, Madrid, Spain

Report:

Our scientific interest is focused on the WC materials and WC-Co system in particular. CCs are used in mining and cutting tool industry because of high hardness and fracture toughness. They comprise the very hard, ceramic WC phase bonded together by a tough 'binder phase' which is cobalt in all of our current research. Our past research revealed superior homogeneity and better wear performance of the recycled materials compared to equivalent grades of new materials. The reason for this has never been properly understood. We believe that the binder metal contains trace elements that are altering its crystal structure and the physical and mechanical properties of the composite material. For example, dissolved impurities in the binder metal could alter its mechanical properties, in quantities too low to be detected by conventional means. The mapping and quantification of these elements was of interest to us.

Therefore, the main aim of our study was to characterize the WC-Co cross sections (prepared using FIB-SEM, and mounted on a TEM grid) in order to improve understanding of the zinc recycling process and identify the locations, distribution and quantity of introduced impurities. The goal being to ultimately improve the industrial production of carbide components using recycled powders. The information obtained using the XRF technique on

the ID16B beamline has already assisted us in understanding these materials, with publications currently planned for this work. Furthermore for us at the Materials Research Department of iThemba LABS is very important to continue with experimental work in this area since we have programme objectives that need to continue. Unfortunately the nuclear microscopy that we normally do with proton microprobe is no longer available at our laboratory since the 6 MV Van de Graff Accelerator was de-commissioned at the beginning of 2016. Thus, we were immensely grateful to the ESRF for this opportunity.

Our shifts were performed successfully in one visit to the ESRF, between the 15th and 19th of May 2017. The TEM samples were successfully mounted onto the sample stage at ID16B, and a pink beam operation mode ($\Delta E/E \sim 10^{-2}$) at 17.5keV with 10^{11}ph/sec was used. We used our first shift for basic setup and alignments, after which we began to map our 6 samples. We finished mapping all of the samples in the allotted time; however we experienced some problems with high dead time caused by the copper TEM grid and the tapered thickness of the samples. The samples were ion-milled to achieve a thin wafer / cross-section, and thus the edges of the samples were significantly thicker than the center. Nevertheless, we were able to obtain full elemental maps of the areas of interest. It should be noted that we were incorrectly instructed by the beam scientist to use fast curing glue (super-glue / Loctite) to mount our samples, which caused signal interference on our first data. Fortunately, we had a second set of backup samples – so no harm was done – but if we had not, the entire trip would have been wasted. Therefore, we would kindly recommend very careful instructions be issued by the beam scientists regarding the use of adhesives.

The use of the PYMCA software has proven very difficult for the uninitiated; therefore a collaborative team meeting has been arranged for the first week of October 2017, in Cape Town, South Africa. At this meeting, all data will be analyzed and a paper prepared for publication by our team. Nevertheless, some preliminary results and observations are presented below.

This Summary of preliminary results must take into consideration three factors related experimental parameters that are not well known from the ID16b line.

1) To be able to accurately input the solid angle in PyMCA we need an accurate value for the distance from each detector crystal and the point of interaction on the target surface/volume.
2) The dead time correction for each detector is not clear as explained by the beam scientist.
3) There was no detector to measure the x-ray probe flux after the target. Then we have to rely on the Io – value measured before the target
4) By previous ID16B line published reports we know that the line was not fitted with a collimator to reduce the halo effect on copper. Of course the samples were mounted in a copper grid for TEM but if the X-ray beam was properly collimated we could have used the data for Cu as well if we wished. With the current optics at ID16b we can't unless the grid was carbon. (We may do this for the next experiment on ID16B)

Aside from the problems of experimental parameters values for quantitative evaluation, in general the quality of the experimental data collected on the 6 samples for cemented carbides by micro-XRF at ID16b line was excellent, matching a very close lateral resolution obtained by TEM analyses. Qualitative results are presented in Figure 1.

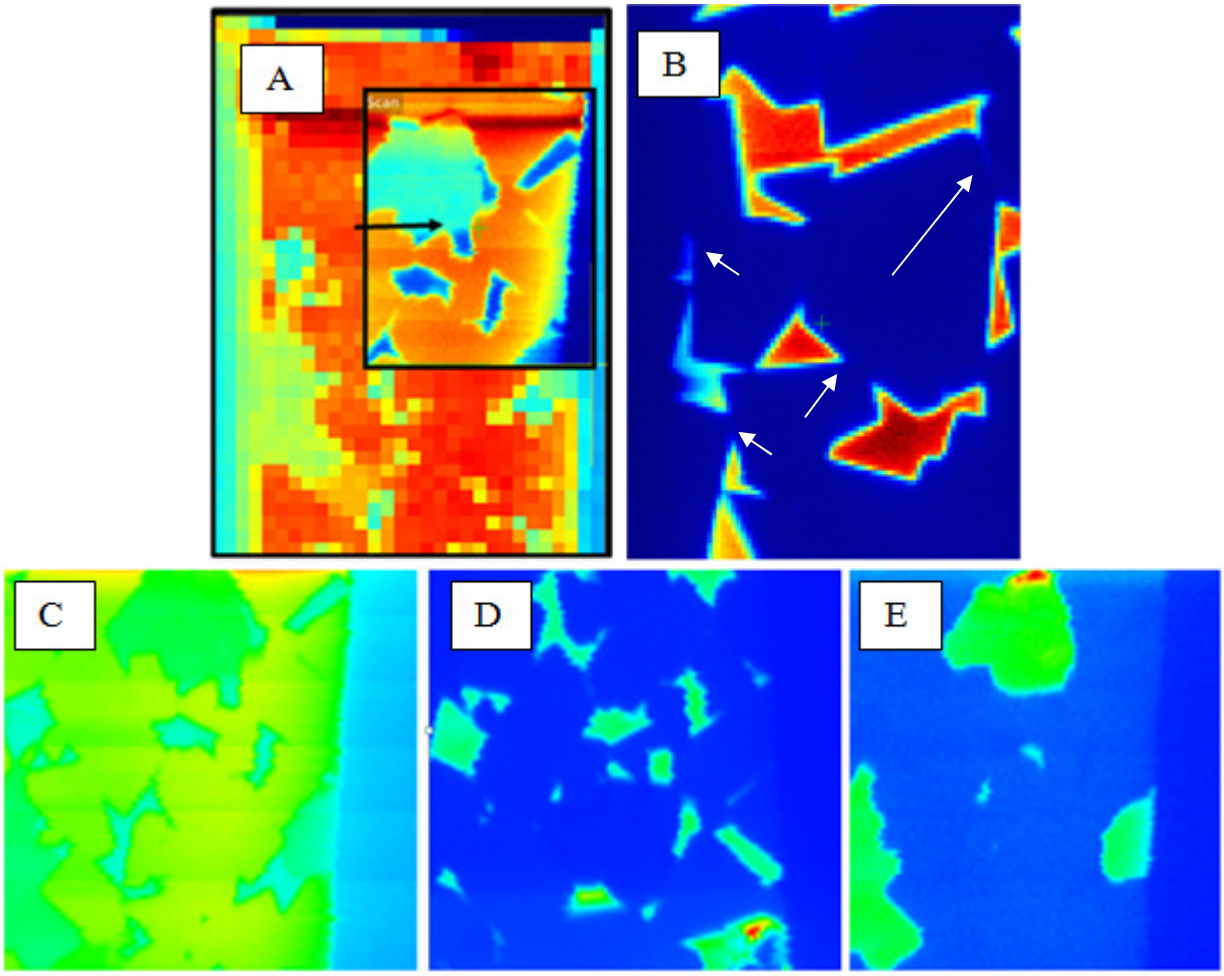

Figure 1: qualitative elemental maps for: A: sample TG2 (twice-recycled, tool grade material) showing a zoomed in area of interest on the initial scan. B: An example of a Co map, showing fine filaments between the cobalt concentrations, indicated by the arrows. C, D and E: W, Co and Ti example maps for sample TG2.

We obtained elemental maps of W, Co, Fe, Ti, and Ta in a zoomed out condition (approximately 10µm x 10µm areas), followed by zoomed-in areas of interest, as shown in the Figures. We intend to analyze this in detail, to see if other impurities were carried into the grain boundaries with the extremely fine cobalt layers. Surprisingly low tungsten concentrations in the cobalt metal binder were observed. Although our results are not yet quantitatively interpreted, and thus must be confirmed, this suggests that tungsten dissolution into the cobalt binder is probably not the main mechanism for improved wear performance of recycled tool materials – which we had initially suspected. To summarize, we did not see a large W diffusion gradient into the binder in any of the materials, and the binder metal of recycled materials resembled that of the new materials. Therefore, this work has aided us in our search for the improved performance of recycled tools, and allowed us to refine our theories. The network of fine cobalt 'threads' running between the cemented carbide grains –

connecting cobalt grains to each other, is something we have never observed before, and is noteworthy and will be published.

In general we obtained the following results, which will be published in future after quantification is complete, but are briefly summarized here (note that the data taken is still being analyzed):

- Tungsten diffusion gradients:
  - We did not observe a diffusion gradient into the cobalt metal, rather the W is quite homogeneously dissolved in the cobalt
  - Since W is a hardener of the binder, we need to look elsewhere for our improved wear performance in the so called 'mining grade' materials, as both new and recycled materials showed similar W-Co solutions. We are now suspecting strain effects.
- Cobalt filaments:
  - We detected cobalt filaments joining cobalt binder grains to each other along WC grain boundaries. These are potential toughening mechanisms and the purity of the cobalt in these areas will be of focus in quantification.
- Ti, Ta and Nb distributions:
  - We have been able to map the distribution of these elements qualitatively thus far. In 'tool grade' materials, and will be able to compare the concentrations of these elements in the binder phase of the new and recycled materials. These elements typically increase the wear resistance of carbides; hence their presence in the binder phase needs to be carefully quantified.