

**THE INDUSTRIAL VIABILITY AND CHARACTERIZATION OF WC-
Co ALLOYS PRODUCED BY ACID LEACHING AND RECYCLING
TECHNIQUES**



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DECLARATION

I declare that this thesis is my own unaided work. It is being submitted to the degree of Doctor of Philosophy in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other university.

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..... day of Year

ABSTRACT

In the current study, the well-established zinc recycling process and a prototype acetic acid recycling plant were successfully employed to recycle cemented tungsten carbide scrap material for re-use as production powders. The recycled materials were studied and compared to new materials at each stage along the cemented carbide manufacturing route, in a production environment. Analysis of by-product materials from the zinc recycling process revealed that while some by-product material can be readily converted into powder using the supplementary acetic acid method, the rest is most efficiently recovered by using a second zinc recycling run and by controlling the size and purity of the scrap material introduced into the process. Various analytical techniques, including the novel use of proton induced x-ray emission studies were used to characterize the materials in both the powder and sintered form. The analyses revealed that the recycled materials possessed superior microstructural homogeneity than new materials, and greater than 99% purity. Studies of milling behavior and slurry rheology revealed no adverse effects of using recycled materials, provided that the slurry properties prior to powder spray drying were appropriately controlled. Polymer binder integrity remained intact despite the longer milling times associated with the use of recycled materials, and the superior slurry stability of recycled materials was demonstrated. The flow behavior and powder rheology of the spray dried powders was found to depend on the precursor slurry rheology and particle grain size. This was controlled predominantly by the formation of a sufficient yield stress to produce ideal, dense granules for greater ease of manufacturing, in both new and recycled powders. The acetic acid recycling technique can be used as a complimentary recycling process to the existing zinc recycling process, and can produce useable recycled material at low cost.

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LIST OF ABBREVIATIONS, SYMBOLS AND ACRONYMS

PRZ - process of recycling with zinc (the zinc process)

SEM - scanning electron microscopy

EDX - energy dispersive X-ray spectroscopy

XRD - X-ray diffraction

ICP-OES - inductively coupled plasma optical emission spectrometry

Micro-PIXE - proton induced X-ray emission studies using a proton micro-probe

W_L - designation of a micro-PIXE map generated from interaction with the tungsten 'L' electron energy level.

HV - Vickers hardness

μm - micron (micrometer)

wt% - weight per cent

h - time in hours

s – time in seconds

°C - degree Celsius

Pa / kPa – pascal / kilopascal

mbar – millibar (unit of pressure)

M_n - number average molecular weight

M_w - weight average molecular weight

PDI - polydispersity index

Mv - mean volume particle diameter

D10 - particle size diameter below which 10% of the particles fall

D50 - particle size diameter below which 50% of the particles fall

D90 - particle size diameter below which 90% of the particles fall

Powder rheology acronyms:

BFE - basic flowability energy, mJ. The energy needed to displace a conditioned powder sample during downwards testing (compression) using the bulldozing action of the rheometer blade.

SE - specific energy, mJ. The energy associated with the lifting action of the rheometer blade during upwards testing and therefore this energy is a measure of powder cohesion.

SI - stability index, defined as the factor by which the flow energy changes when the powder is repeatedly tested.

FRI - flow rate index, defined as the factor by which the powder flow energy changes when the rheometer tip speed (flow rate) is reduced by a factor of ten.

NBFE - normalized basic flowability energy, mJ/g. Accounts for the differences in powder masses between samples, by taking the quotient of BFE and the powder sample mass, yielding a measure of the energy needed to move each gram of powder.

1. INTRODUCTION

1.1 Research background and motivation

One of the most important processes upon which our society and economy is built is the mining and manufacturing industry, in which recycling is becoming increasingly important because of high raw material costs and depleting mineral reserves. The manufacturing and mining industries are extremely dependent on hard materials capable of drilling and crushing rock, cutting and shaping metals, processing minerals and fabricating a wide range of materials. One such hard material is tungsten carbide (WC) and its alloys, collectively known as 'hardmetals' or cemented carbides. These alloys comprise of the hard tungsten carbide phase cemented by a strong and tough metallic binder phase (usually cobalt (Co), but sometimes iron or nickel) which produce a final product possessing high hardness and moderate toughness [1].

Cemented carbides account for approximately two thirds of the world's tungsten consumption and if present production volumes continue, the world's tungsten resources could be depleted in 40 years [2]. Recycling of cemented carbide materials is usually energy intensive and environmentally unfriendly [3] and each recycling method carries advantages and disadvantages.

The zinc reclamation process [4, 5] is widely used in hardmetal recycling because it is relatively straightforward and convenient, but requires large vacuum furnaces and has a high electricity consumption, the material chemistry and composition can change, and the material to be recycled does not always break down into powder in the first recycling run. The zinc recycling process has been the subject of ongoing research interest in recent years [5].

Acetic acid leaching is a method of cemented carbide recycling that can be conducted at low temperatures, and pressures and leaches out the cobalt binder from between the tungsten carbide grains, leaving a brittle ‘carbide skeleton’ that can be further comminuted by mechanical means [3]. The process allows for the cobalt to potentially be recycled, as well as the possibility of reclaiming and recycling the acetic acid, allowing it to be used again for further leaching procedures; hence this is considered an environmentally friendly technique. To the author’s knowledge, the acetic acid method has never been utilized for recycling on an industrial scale. Previous laboratory-scale studies into acetic acid recycling indicated that the process is slow (taking several days to several weeks depending on the material) to leach fully dense cemented carbide components, even under ideal conditions such as the addition of oxygen and pressure to the reaction vessel [3, 6, 7]. It is for this reason, that the process was likely never industrialized.

The zinc recycling process, while much quicker to perform than the acetic acid method, produces a porous by-product or so called ‘oversize material’ which requires a second recycling run to reduce to powder, thereby increasing production costs. Hence, in this work, the acetic acid process has been investigated as a possible supplement to the zinc recycling process, to be used for recycling the by-product material rather than subjecting it to a second zinc recycling run. The large surface area of the porous by-product material from the zinc process should allow for a more rapid reaction rate than leaching dense cemented carbides.

Efficient use of recycled materials in industry is highly relevant as it can lead to less dependence on large quantities of newly mined and synthesized material. Additionally, new and recycled materials cannot be assumed to behave identically during manufacturing, and unexpected behaviour differences could lead to manufacturing downtime and/or unforeseen operational costs. Hence, detailed analyses and comparisons were performed on new, zinc recycled, and acetic acid recycled materials across the full cemented carbide manufacturing process. The

project focused on a WC-6wt% Co cemented carbide composition due to its abundant use in the mining industry and availability of material.

1.2 Research aim and objectives

The goal of this project was to determine the industrial impact, production implications, and material differences when using zinc recycled, acetic acid recycled and new (as-synthesized and as-supplied) cemented carbide materials.

The objectives of this research were to:

- Assess the impact of using new, zinc recycled and acetic acid recycled WC-6wt% Co materials across the entire manufacturing process in a powder production environment.
- Evaluate the advantages and disadvantages of each recycling method compared to new powders.
- Perform a simple cost comparison to compare the efficiency and cost of the zinc recycling process, the acetic acid process, and new material.

1.3 Contribution to knowledge

For the first time, zinc recycled, acetic acid recycled and new materials have been compared with each other in detail, at each step of the manufacturing process and across an entire production line. Experiments such as this, on a production scale, are rarely possible and seldom reported in materials engineering research. The study begins with raw materials, followed by milling behaviour, slurry rheology, spray dried powder properties and rheology, pressing behaviour and finally sintered alloy properties.

Highlights of the most significant and novel contributions include:

- The acetic acid method was investigated as a supplement to the zinc recycling process. A pilot plant was designed, constructed and used to produce acetic acid recycled materials on a production scale.
- The powerful proton induced x-ray emission technique was used to compare and characterize recycled cemented carbide materials, which revealed that zinc recycled cemented carbides have a more homogeneous microstructure than new materials, and was able to map the location of impurities within the microstructure down to ppm levels of accuracy.
- By-product material resulting from the zinc recycling process was investigated in detail, and mechanisms for the formation of the types of by-product were proposed. Recommendations were made for further industrial optimization of the zinc process.
- Slurry rheology results showed that recycled slurries tend to be more stable in a suspension which directly impact the slurry rheology and therefore the shape, structure, powder rheology and behaviour of spray dried powders. The results of this work therefore allow for better control of recycled slurries in production, to produce optimum recycled powders and less waste.
- Detailed and novel powder rheology and compaction comparisons of new and recycled cemented carbide powders were performed which uncovered an optimum size and particle distribution for each powder, as well as the behaviour and performance of such powders in a humid environment.
- The metallurgical properties of various zinc recycled, new and acetic acid recycled grades were compared and contrasted, which showed that the recycled materials were able to produce alloys which meet the required metallurgical specifications for mining applications.
- A simple financial analysis of the processes was performed, to compare the processes and assess the industrial viability of each technique.

As our world becomes more environmentally conscious, this study involving the production implications of recycling techniques has been directly relevant to the cemented carbide industry. The understanding gained in this work is expected to

lead to greater use of recycled materials in future; hence this project has achieved scientific, industrial and environmental significance.

At the time of submission of this thesis, 5 scientific papers have been published in ISI accredited journals with another in preparation. Further details on the research outputs achieved are provided in the appendix.

1.4 Layout of the thesis

Following this introductory chapter the thesis begins with a literature review which provides background, focus and places the project in context in this field of materials research. The literature review is followed by the research methodology chapter which outlines the range of materials experiments and analyses performed in this work. The results sections proceed from the initial studies of micro-PIXE as a technique in cemented carbide characterization, to the evaluation of zinc recycled by-products. The impurity identification in new and recycled powders is then presented, followed by the results of the acetic acid leaching experiments. Thereafter the slurry and powder rheology sections explore the flow behaviour of the powders, followed by simple powder pressing test results. Microstructural and material properties of the sintered alloys are then provided. In the discussion chapter the results are critically analysed, with the main research findings presented in the conclusions chapter. All published work cited is provided as the final chapter of this thesis.

1.5 Scope and limitations

This research studied the production implications and metallurgical effects of recycling on WC-6wt% Co alloys. It did not undertake alloys of different cobalt or alternative binder proportions and compositions. Although cubic carbides are

added to hardmetals when used in the manufacturing industry, the focus of this work was to investigate a standard mining grade composition, thereby laying the foundation for expanded future research on cubic carbide materials, and materials of varying binder composition.

2. LITERATURE REVIEW

2.1 Hardmetal manufacture and properties

2.1.1 Introduction

In 1896, W_2C was first synthesized followed by tungsten monocarbide (WC) two years later [8]. Due to the brittleness of these carbides, they did not find commercial use for many years. It was only much later in the 1920's, when experiments into the infiltration of carbide materials with various iron group metals were performed, that a renewed interest in these materials arose [8]. Although several binder metals, used to bind the hard tungsten carbide grains together with a tougher cementing agent were investigated, cobalt was determined as the best binder metal because of the good wettability of WC and Co. Cobalt is still the dominant cemented carbide additive to this day. Not long after the introduction of cemented tungsten carbides, additions of cubic carbide phases, such as titanium carbide (TiC) and tantalum carbide (TaC), were introduced [9]. The cemented carbide group of materials were found to possess high hardness, abrasive wear resistance, high deformation resistance chemical inertness, a high stiffness and a moderate fracture toughness [1, 10-13], which has led to their use in many industrial applications, such as cutting tools, wear parts, mining components, nozzles, extrusion dies, and many more applications [14-17].

2.1.2 Powder production

Cemented carbide powders are produced using powder metallurgical techniques. The raw material powders include predominantly finely divided tungsten carbide

and cobalt, with other binder metals such as nickel or iron and other metallic phases used less frequently [11, 18-21]. Cubic carbide additions are commonplace in order to improve the wear resistance of cemented carbide substrates in cutting tools [22], the addition of which depends on the required properties of the cutting tools [23].

Milling is used to break down and blend the powders so that the binder metal and other additives are homogeneously distributed. Cobalt has an advantage over alternative binders such as nickel and iron because it can mill down to an extremely fine size [24]. A liquid phase such as ethanol, heptane or acetone is used during milling to minimize heating, reduce oxidation and allow for the production of a slurry to facilitate powder granulation in the form of spray drying [25]. A small amount of paraffin wax or similarly behaving organic binder such as polyethylene glycol, is added and milled with the powder to facilitate pressing, reduce die wear and to strengthen the ‘green’ compact prior to sintering [24]. It also provides a protective coating for the powder particles that reduces oxidation and improves the pressing properties of the powder [25]. The slurry is then spray dried in a hot inert atmosphere, usually nitrogen, to produce spherically shaped, free flowing, powder granules. The free flowability of the spray dried powder allows for repeatability of powder die filling and density during compaction, in which the powder compact is pressed into the required shape prior to sintering [25].

2.1.3 Sintering

In conventional WC-Co alloy sintering, the organic binder is removed by heating the material to around 500°C in a hydrogen atmosphere, after which the batch is heated to its final sintering temperature, ranging from 1300°C to 1600°C [24, 25]. The sintering parameters are varied to achieve the desired microstructure and properties based on the grain size, cobalt content and additives present [23]. The sintering process is shown in Figure 2-1.

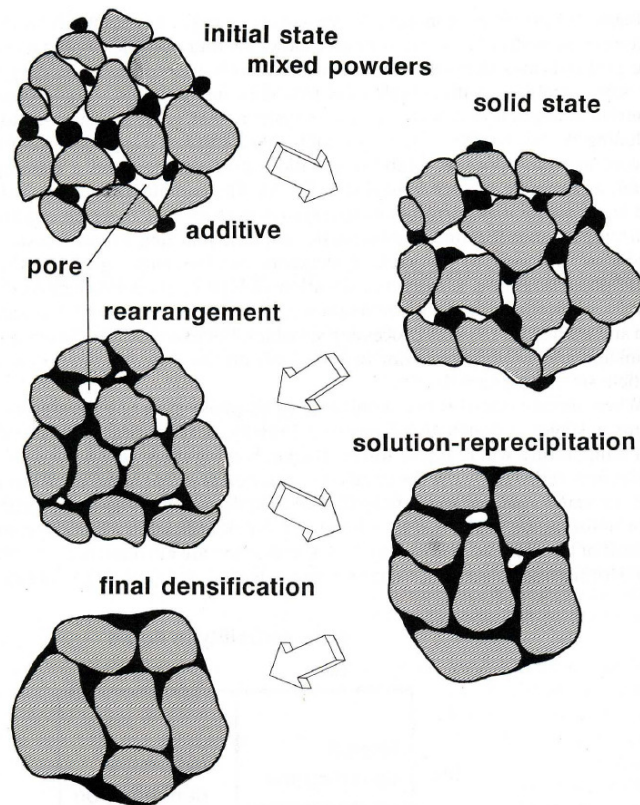


Figure 2-1 The different stages of the sintering process [26].

The compacted powder is heated to a temperature sufficient to melt the binder metal, hence WC-Co alloys densify by a liquid phase sintering process. The melting of the binder metal draws the WC grains closer together. Although some solid state sintering occurs, the sintering process in cemented carbides occurs predominantly in the liquid phase. The carbide phase partially dissolves in the Co, lowers the melting point of cobalt, and re-precipitates upon cooling, owing to the decrease of its solubility in cobalt with decreasing temperature [24, 27]. It has been shown experimentally that the rejected WC crystallizes onto the surfaces of the undissolved WC grains still present, hence resulting in grain growth of these particles preferentially [24]. The shrinkage of the cemented carbide component increases as the sintering temperature is increased and reaches a maximum between 1300°C and 1350°C. The porosity disappears at these temperatures largely because of the presence of the liquid cobalt, under the influence of surface tension of the binder metal and the good wetting of WC by Co. It is the good wetting of WC by Co that leads to the strong bond between the phases and

consequently the success of WC-Co alloys compared to alternative binders [26]. Cemented carbide alloys usually experience a linear shrinkage of 17 to 25%, resulting in products of high density and very low porosity [25].

2.1.4 Material properties

In order to control the properties of cemented carbides, the production history of an intermediate manufacturing step has great importance to the following steps - more so than in conventional metal production [10]. If an improper ingredient or method is used, it dictates the properties of the final product, and cannot readily be rectified in a subsequent processing step. Hence, testing in cemented carbides comprises two categories [10]:

- Raw material and powder production testing (everything prior to sintering)
- Sintered property evaluation

Raw material testing includes chemical purity, powder density and size distribution and oxidation state. Production testing of powders during the cemented carbide manufacturing process include particle size analysis, slurry characteristics, powder flow and density, powder morphology and bulk properties, pressing behavior and green strength and density and pressing defects. The sintered properties that are typically tested include density, hardness, fracture toughness, transverse rupture strength, abrasive resistance, magnetic properties and microstructural analysis [10].

The main phase in simple cemented carbide alloys is WC which has a hexagonal crystal structure, while the cobalt binder can appear in two crystal structures namely hcp (hexagonally close packed) and fcc (face centred cubic) [9]. A section of the ternary phase diagram of a WC-6wt% Co alloy is shown in Figure 2-2 [22, 28]. Usually, the cobalt binder in cemented carbides exists in the fcc state,

because the W and C dissolved in it restrict the fcc to hcp phase transformation. An increase in the amount of carbon in the alloy, results in a decrease in the amount of W dissolved in the binder [9] and vice versa. From the phase diagram in Figure 2-2, it is clear that WC without graphite (free carbon) or eta phase formation, occurs within a narrow window, between 'a' and 'b' marked on the phase diagram, which correspond to 5.68 and 5.77wt% C in the alloy [22].

The continuous skeleton of tungsten carbide grains is filled with the cementing agent (cobalt) - hence grain size plays an important role in the microstructural properties, determining the size of the binder 'pools' or mean free path and contiguity [9].

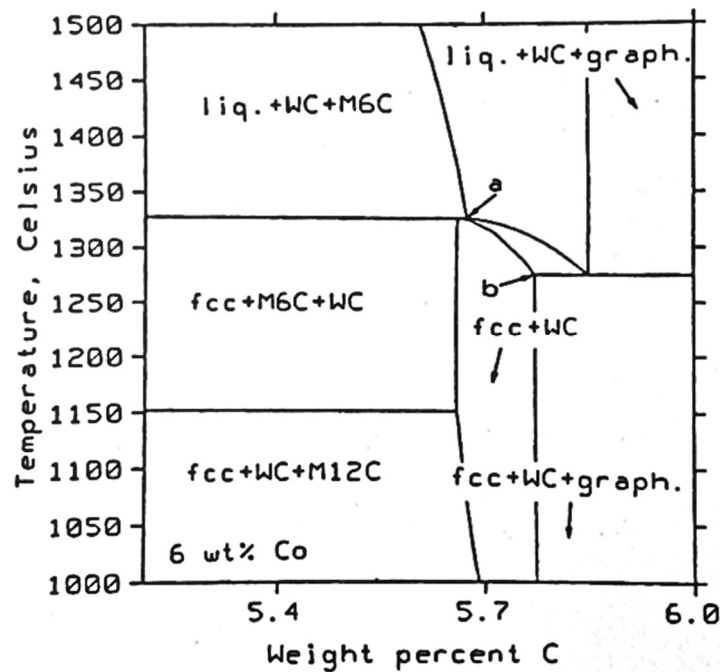


Figure 2-2 Section of the W-C-Co ternary phase diagram for WC-6wt% Co, M6C and M12C refers to eta phase carbides, and fcc refers to the cobalt phase [22, 28].

Hardness is the most important requirement for hardmetal applications, and is readily influenced by: grain size, porosity, structural variations and phases present (such as those related to carbon content) in the alloy [29]. Hardness of cemented

carbides is usually measured in Vickers hardness, using a pyramidal diamond indenter, or Rockwell A hardness which makes use of a hemispherical / cone shaped indenter [10].

Magnetic property testing includes coercive force and magnetic saturation readings and are used in the cemented carbide industry to assess the quality of the material [30]. In order of importance, the factors that influence magnetic saturation are: the amount of cobalt present in the sample, a binder mean free path and then the contiguity of the cemented carbide grains [31]. The magnetic saturation indicates the W concentration in the binder metal quantitatively, as well as the overall carbon content [30]. Coercivity provides qualitative information of the WC grain size, and can readily be influenced by other factors such as the residual stress distribution in a sample [10, 30, 32].

The magnetic saturation of WC-Co of known Co contents depends only on the W concentration dissolved in the binder, which occurs in response to the overall C content [30] and is used as a standard quality control technique in cemented carbide manufacturing to assess the carbon level for a grade of known cobalt content [10]. The influence of cobalt content on the magnetic saturation in WC-Co alloys is shown in Figure 2-3, with the associated coercivity of the different grades [31]. Coercivity measurement can yield an approximation of within 5-10% error when used to calculate grain size in simple WC-Co alloys, provided that it is used to test unused components, and not those exposed to testing which can contain residual stresses [30].

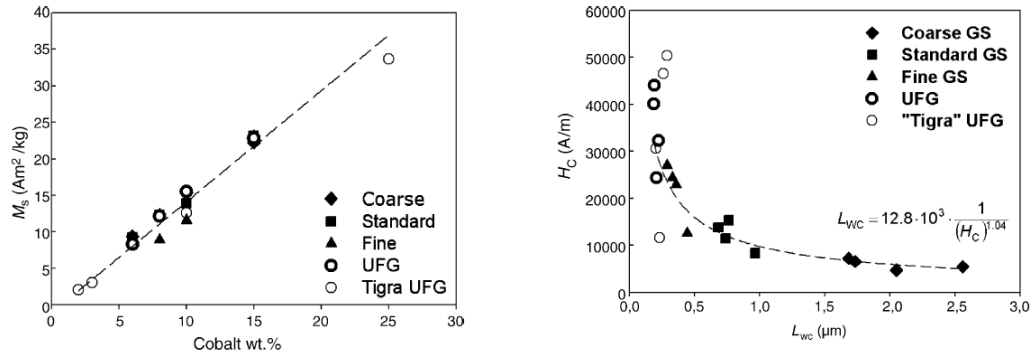


Figure 2-3 A: The influence of Co content on the weight specific magnetic saturation (M_s) for different WC-Co grades. UFG refers to ultra-fine grained material. B: Coercivity vs. WC grain size [31].

2.2 Cemented carbide recycling

2.2.1 Introduction

Numerous methods have been developed to recycle cemented scrap materials. According to Paul [33], cemented carbide recycling can be subdivided into two general categories, namely removal of the binder metal using a selected process, leaving a finely divided carbide matrix behind (skeleton-like, framework structure) or by chemical modification methods that convert the carbides into a different form, for example into oxides. The general range of methods are reviewed in the following section. Because zinc recycling and the acetic acid leaching technique are focal points of this research, they are listed as independent sections with a detailed review.

2.2.2 Recycling techniques

The two broad categories of cemented carbide recycling can be refined into more specific fields of categorization, based on the primary technique used in each method. These fields are:

- Acid or leaching recycling methods
- Electrochemical means
- Oxidation / chemical modification techniques at high temperature
- Impingement or blast techniques
- Liquid metal infiltration techniques e.g. the zinc process
- Hybrid methods (combinations of the above)

There are several patents and publications relating to acid leaching technology in cemented carbides. Kinstle et al. [1] describe a method of recovering tungsten, vanadium, chromium and molybdenum metals from carbide metal scrap by using an alkali metal hydroxide which is then heated in the presence of oxygen at an elevated temperature and pressure for a period of time sufficient to form a water soluble alkali metal hydroxide. The metal is then recovered from the water soluble alkali metal salt using chemical means. According to Seegopaul et al. [34], cemented carbide materials can be reclaimed by oxidizing scrap into tetragonal and octahedral tungsten trioxide which is insoluble in water with a neutral pH. This material is digested in an acidic solution that selectively dissolves the cobalt and not the tungsten. Cobalt hydroxide and oxychloride are precipitated out of solution by raising the pH to between 6 and 10. The tungsten and cobalt compounds are separated from the slurry and re-dissolved in an aqueous solution having a pH greater than 11. The product is spray dried and carburized as necessary.

Coatings can present significant problems for leaching processes because they act as a physical barrier to diffusion and chemical interactions. Reilly [35] patented a process utilizing azeotropic solutions of hydrochloric acid to permeate alumina

(Al₂O₃) coatings and dissolve the underlying binder material to yield a depleted tungsten carbide framework which remains covered (at least in part) by the coating. The carbide framework can then be oxidized and carburized back into WC, or exposed to further processing steps e.g. the formation of sodium tungstate. This method, however, requires the subsequent separation of the coating by some other means.

Hydrothermal techniques have also been investigated by various researchers [36] in which the cobalt binder is extracted by using hydrochloric acid at 110°C, and subsequently pulverized due to the brittleness of the carbide framework or 'skeleton' that remains behind, using ball milling. Oxidation was found to occur more easily on these materials (probably due to activated / fresh surfaces and reprocessing procedures) which were found to degrade the properties of the resulting materials. Hydrochloric acid treatments appear to be favoured among several researchers. Ritsko et al.[37] and Reilly [35] utilized HCl as the leaching agent. Phosphoric acid leaching techniques have also been attempted by some authors [38, 39]. Tungstic acid is another method described by Brookes [40] who investigated a leaching method that produces ammonium paratungstate.

Several authors have developed methods to recycle cemented carbide scrap using electrochemical means. Usually such techniques involve direct oxidation of the WC at the anode of an electrochemical cell that usually produces an insoluble product [38, 39, 41-44]. In the case of Paul et al. [33], this insoluble product is tungstic acid (HCl solution was used as the electrolyte), and cobalt ions enter and then remain in solution, until electrodeposited at the cathode in the cell.

Faga et al. [45] describe the general procedure for oxidation methods of recycling as follows: materials selection based on the desired chemical composition; oxidation at high temperature; milling, followed by seeding; oxide reduction to obtain metals; mixing of the powders with carbon; carburisation at high temperature under a reducing atmosphere; mixing and seeding of powders. Other

sources also use methods of oxidation recycling based upon this type of approach [44, 46-50].

Only one method using blasting has been found in literature. The coldstream process [51] involves a high velocity air pressure stream impinging metals and alloys against a fixed target. The major problems associated with this method include contamination from excessive wear of the machine components, oxidation problems and problems associated with inadequate reduction of particle size, which is why this process was never further developed.

2.2.3 Zinc recycling

The zinc process is the most widely used recycling process in the cemented carbide manufacturing industry. It is commonly referred to as 'PRZ', an abbreviation for the 'process of recycling with zinc'. This method, originally invented in the 1970's, has experienced renewed interest since 2005 (when global tungsten prices increased) as it is the most cost efficient and environmentally friendly recycling method. Prior to 2005, only 20 to 25% of hardmetal was recycled in Europe, but today the recycling ratio stands closer to 50% [5].

When using the zinc process, scrap material is sourced, sorted and then packed into graphite boats or crucibles along with zinc. A schematic of this process is shown in Figure 2-4. The furnace is evacuated of air, filled with argon and heated to temperatures ranging from 750°C up to 960°C, depending on the details of the process such as furnace used, nature of the scrap etc. [4]. Treatment of the carbide with molten zinc at these temperatures results in a liquid alloy formation of the zinc and the cementing agent, hence, when the zinc is removed by distillation, the resulting product consists of a mixture of the carbide and the cementing agent in which the bond between the two has been broken [4, 5, 52]. The zinc vapours are recovered by condensation (distillation) in a cooler zone of the furnace. The weight ratio of zinc to binder metal (usually cobalt) used in the zinc recycling

process ranges from 30:1 to 10:1 with a preferred range of 15:1 or 20:1. The time required for the treatment depends on the size and shape of the scrap objects [4]. The zinc is pulled through the carbide scrap by a powerful vacuum and distilled, and can be recycled again. The resulting product consists of a mixture of the carbide and the cementing agent, which is easily broken down by mechanical means to a particle size similar to that of the grain size of the sintered cemented carbide microstructure (before recycling).

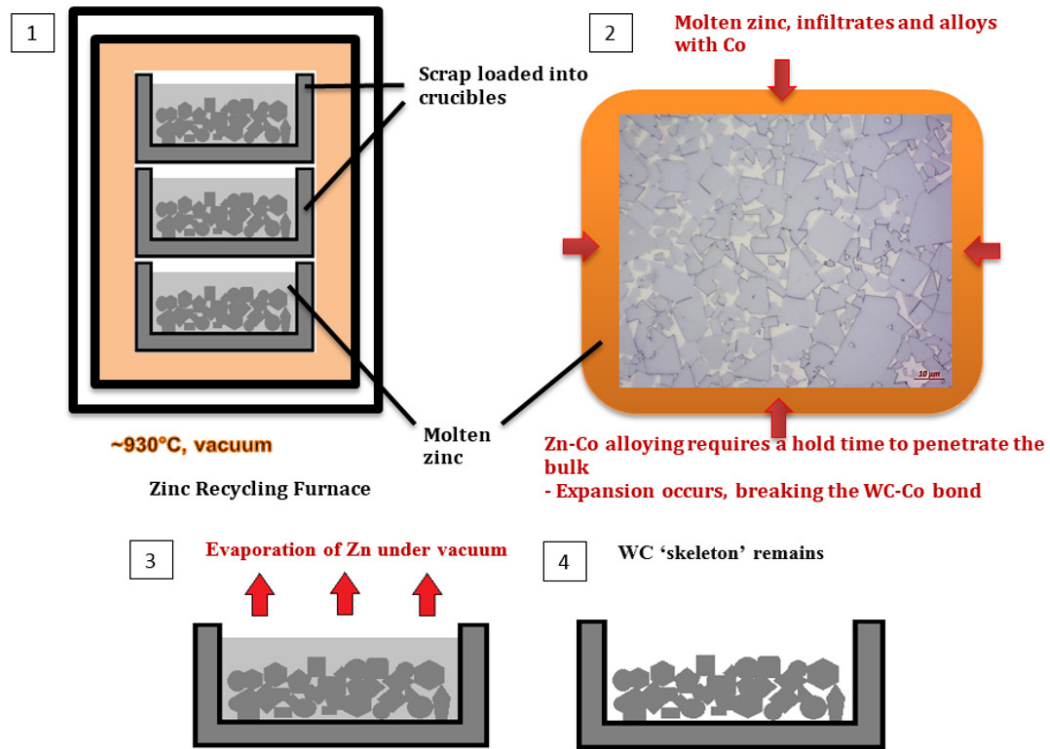


Figure 2-4 Schematic of the zinc recycling process. 1: The scrap is loaded into crucibles, the furnace is evacuated and raised to a temperature $> 750^{\circ}\text{C}$, 2: The zinc infiltrates the binder metal, 3: the zinc is evaporated and distilled, 4: an expanded WC-Co 'skeleton' remains.

Karumaa and Kurkela [5] studied four different zinc reclaimed grades, mixed with different amounts of new powders with a similar grain size. The cobalt content of all their grades was adjusted to 10wt%. Figure 2-5 A and B show the morphology and cobalt distribution in a recycled, submicron grade powder. Whereas, C and D

show the morphology and cobalt distribution map for a medium grained recycled mining powder, as imaged using a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) mapping [5]. The powders were milled in batch sizes of 300g in ethanol, with some carbon addition due to the zinc recycled powders being carbon deficient. Paraffin was used as the binding agent and was added 4 hours before the end of the mill cycle.

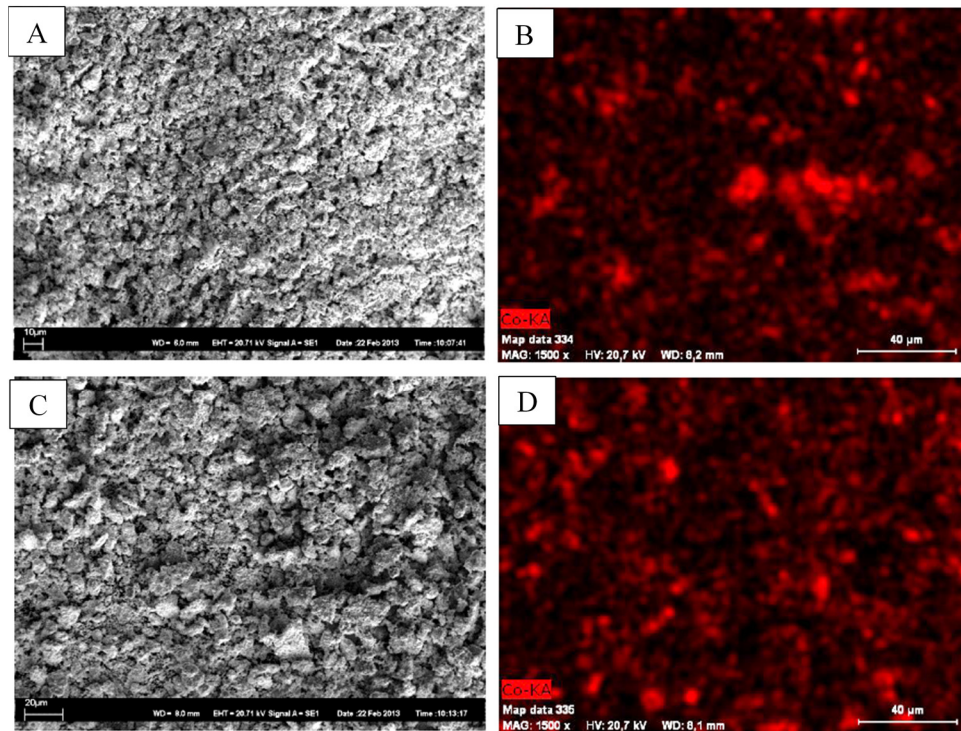


Figure 2-5 A: Morphology of zinc reclaim powder (submicron grade) and its cobalt distribution (B). C: Morphology of zinc recycled medium grained mining grade and its associated cobalt distribution (D) [5].

The powders were vacuum dried, sieved and sintered under vacuum at 1380°C for 1h in the case of the submicron grades (Figure 2-5 A & B), and at 1450°C in the case of the recycled mining / courser grained materials. The team also carried out a larger scale production mill of 250kg that was extruded into WC-Co rod and sintered at 1375°C for one hour.

Karumaa and Kurkela [5] observed that zinc recycled powders obtained a coarser particle size than the new WC-Co materials, when measured using laser diffraction particle size analysis, which they attributed to the agglomerated nature of the recycled powders. Figure 2-6 A and B show their observations with respect to fine grained new (virgin) material and zinc recycled fine grained material, with the zinc recycled material considerably coarser than the new powder ‘equivalent’.

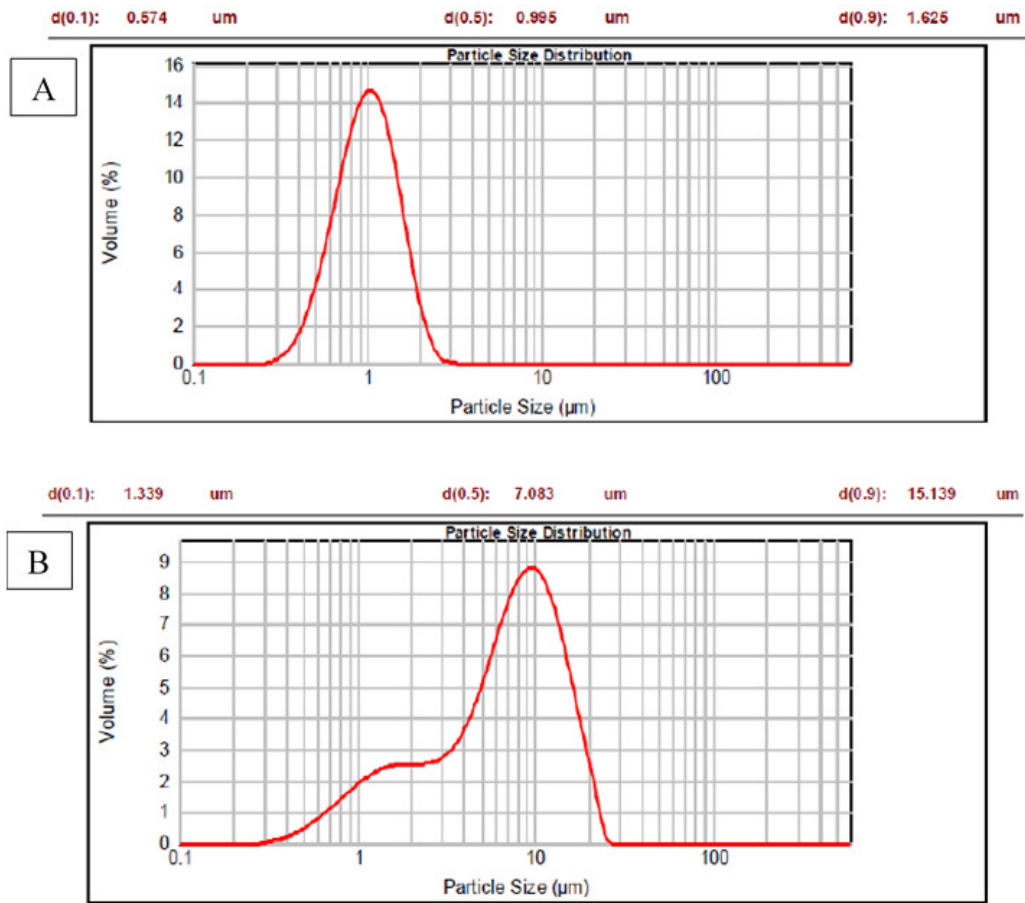


Figure 2-6 A: Particle size distribution of new 0.8 μm WC powder, B: particle size distribution of zinc reclaimed fine grained material [5].

Karumaa and Kurkela [5] used SEM and EDS to analyse the powders for cobalt distribution differences after wet milling and reported no observable difference between the zinc recycled and new powders. They also analysed the sintered microstructures the virgin and blended PRZ + virgin batches. Figure 2-7 shows the sintered microstructures of each grade.

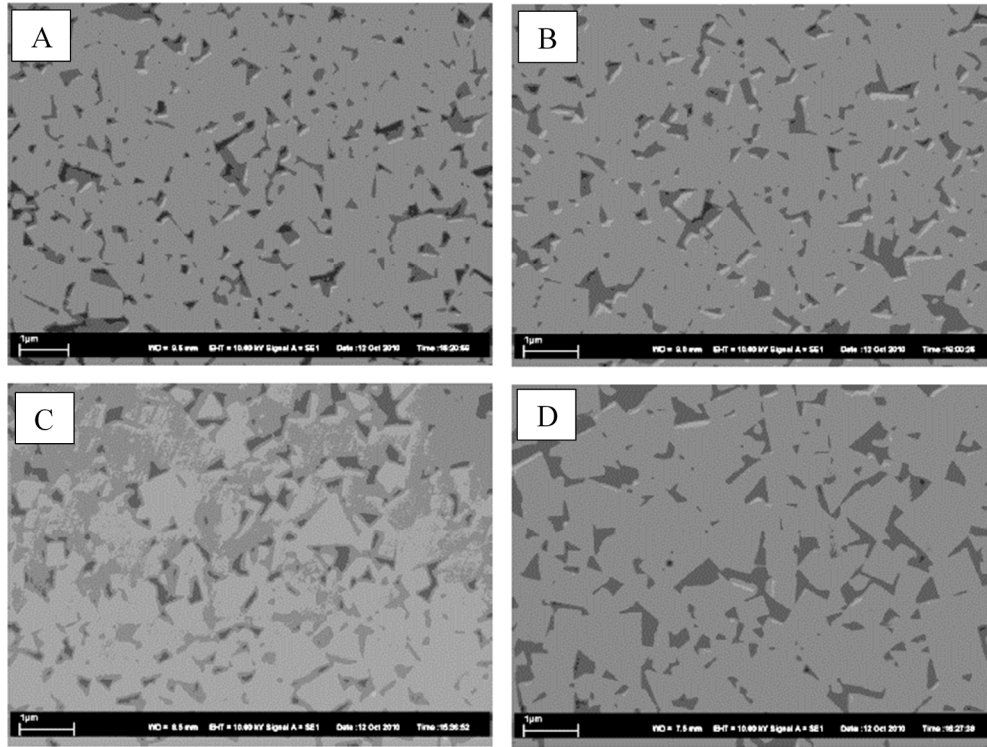


Figure 2-7 A: Virgin 0.65 μ m WC + 10% Co (submicron material). B: 50% virgin 0.65 μ m + 50% zinc recycled submicron material. C: Virgin 0.8 μ m WC + 10% Co, D: 50% virgin 0.8 μ m WC + 50% fine grained PRZ material [5].

When studying the microstructures of the new and zinc recycled materials, Karumaa and Kurkela [5] observed that when using high quality feed materials from the zinc process (without too many contaminants i.e. by careful sorting of the feedstock scrap material entering the PRZ process) the WC grain size distribution and microstructure are comparable and that up to 50% zinc recycled material can be used to blend a batch of fine grained WC-Co alloy. The submicron grades, however, showed some coarseness in the case of the zinc recycled material compared to the new material, but despite PRZ powder additions typically ranging from 20-30wt% in such applications, they suggest that up to 50wt% can be used without compromising material properties [5]. Transverse rupture strength was also measured, and no negative effects of adding zinc recycled material were observed in any of the grades. Density, Vickers hardness and magnetic coercivity were also measured with the results shown in

Table 1. Only a slight drop in hardness with the zinc recycled powders occurred, perhaps because of the grain growth during sintering of the slightly coarser PRZ material, while very little difference in coercivity was observed.

Table 1: Mechanical properties of 2.5 μm + zinc recycled medium grained material, made up to 10wt% Co [5].

Material	Density g/cm ³	Hardness HV30	Coercivity Oe
100% 2,5 μm WC	14,53	1360	138
80% 2,5 μm WC+	14,54	1367	140
20% zinc reclaim			
60% 2,5 μm WC+	14,54	1367	140
40% zinc reclaim			
40% 2,5 μm WC+	14,53	1368	139
60% zinc reclaim			
20% 2,5 μm WC+	14,54	1352	137
80% zinc reclaim			
100% zinc reclaim	14,54	1356	139

From their work, Karumaa and Kurkela [5] concluded that zinc recycled material does not negatively impact the properties of hardmetal alloys provided the feedstock is of high quality and purity. It is their prediction that the zinc recycling process will gain market share in the future and has not yet realized its full potential.

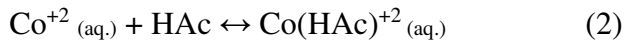
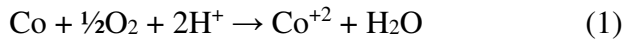
2.2.4 Acetic acid recycling

The predominant research in acetic acid leaching is based on the work of Edtmaier et al. [3] and Meissl [7]. Hardmetal tool scrap and components were submerged in an aqueous acetic acid solution, through which both pure oxygen and air were

bubbled in their experiments [3]. The reason for the oxygenation is explained later, but it is a necessary step to produce a favourable reaction. The process was successfully used to selectively remove (dissolve) the cobalt binder metal from the hardmetal components. Starting composition, temperature, concentration and pressure were evaluated in terms of the time required for complete removal of the cobalt binder phase. In the words of Edtmaier et al.: [3] “Although cobalt metal can be dissolved in many acids, the challenge is to establish an industrial process that does not produce problematic emissions, where the scrap does not have to be crushed before leaching and the reagents can be recycled.” Further mentioned is the fact that operations with other acids e.g. sulphuric, nitric and hydrochloric, have negative environmental impacts and the low pH used results in a lack of selectivity of the acid i.e. it can leach more than just the cobalt, and has the negative side effect of forming tungstic acid which can deposit in the pores of the leached zones.

One approach has been to crush the scrap before acid leaching, but this can lead to significant iron contamination (usually a steel mill is used), which is undesirable. “It is therefore a challenge to establish an ecologically friendly method using hardmetal scrap of original size and shape. Acetic acid and especially aqueous solutions thereof can be a suitable way out” [3]. In their experiments, Edtmaier et al. [3] constructed a laboratory scale, 4 litre, thermostat controlled ($\pm 1^\circ\text{C}$) pressure reaction vessel that was used to investigate the effect of oxygen and air pressure. Oxygen or air was bubbled through the tungsten carbide scrap, and thus the acid, and was constantly circulated through the scrap. Small scrap samples were removed at different times during the experiment, cut, polished and characterized by the thickness of the leached layer using standard metallographic techniques. The thickness of the cobalt or binder depleted zone indicated the degree of removal of binder material with respect to the experimental parameters. Photometric analysis, X-ray fluorescence (XRF) and scanning electron microscopy (SEM) were used to characterize the cross sectioned samples. The ‘shrinking core model’ was used to explain the cobalt leaching kinetics. The researchers found that de-aerated acetic acid was effective only to a certain point,

when the originally clear acid solution changed to a slight pink colour that did not change with time after a certain point. It was found that acetic acid cannot dissolve the cobalt by itself, but rather, dissolves the surface oxide layer. The colour change from clear to pink is the result of cobalt acetate formation. It was surmised that oxidizing conditions must prevail in order to continue with cobalt removal as shown by Equations 1 and 2:



It was found, that with oxidizing conditions of this nature, combined with a temperature of up to 80°C, the dissolution rates of the cobalt binder can be surprisingly high. This results in a magenta coloured concentrated solution of cobalt acetate tetrahydrate as described by Meissl [7]. From Figure 2-8, it is clearly visible that the binder attack begins on the surface of the cemented carbide and proceeds inwards towards the centre [3]. The carbide skeleton maintains the original shape of the scrap material. The carbide skeleton consists of WC and any other carbide additives e.g. TiC, TaC etc., that may be present within the microstructure. During the first stage of the process, the layer thicknesses as well as the concentration in solution are both approximately linear. Further progress was observed, as the cobalt surface area decreased with time, and the thickness of the depleted layer increased. It was determined that the layer thickness can be used to monitor the extent of the reaction [3].

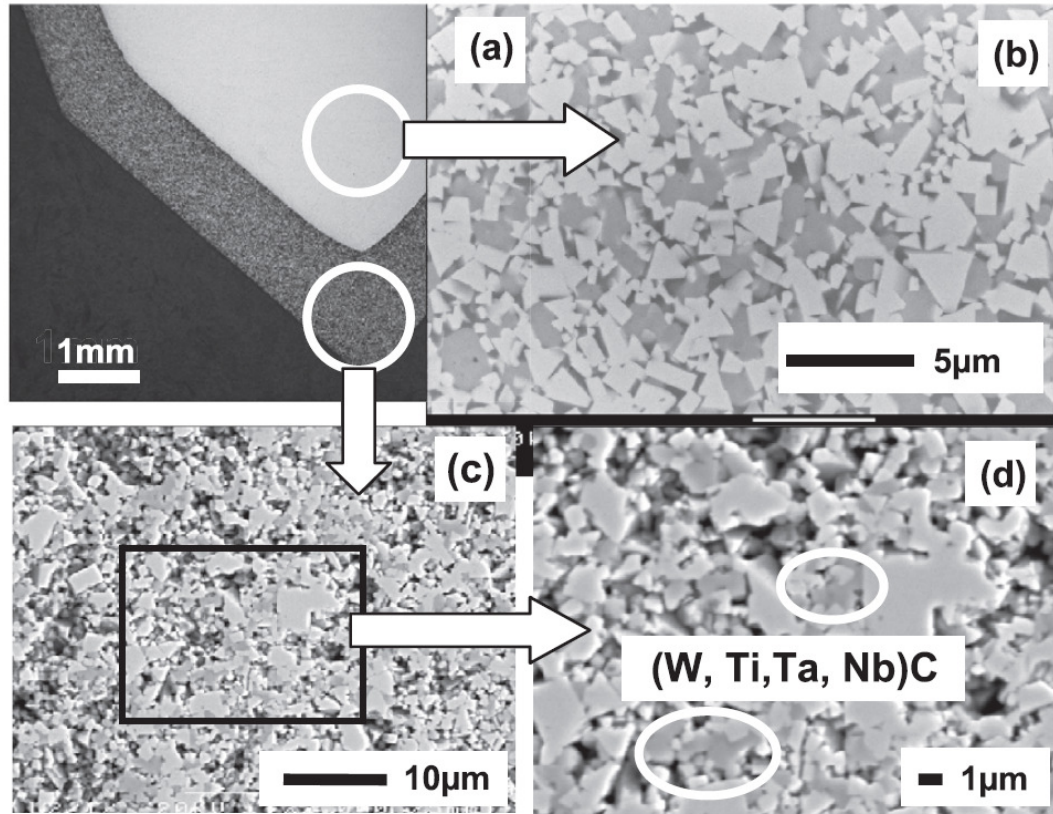


Figure 2-8 Cross section of a partially leached cutting insert. (a) Microstructure of the un-leached core, (b) leached layer (binder depleted zone), (c) and (d) channels of the leached cobalt binder and remaining WC, with (W, Ti, Ta, Nb)-carbide skeleton [3].

Edtmaier et al. [3] used several different concentrations of acetic acid, and reported that complete removal of various scrap types occurred, but with differing times depending on the type of scrap, oxygenation rate, pressure, etc. Figure 2-9 illustrates the progressive formation of the cobalt binder depleted zone. Figure 2-10 summarizes the results acquired by the research team. It can be seen that the maximum dissolution rate is achieved at 80°C and at 5 bar pressure with pure oxygen. Although these are the best possible, i.e. the fastest rates, pressurized oxygen is expensive, as is maintaining a pressure vessel itself.

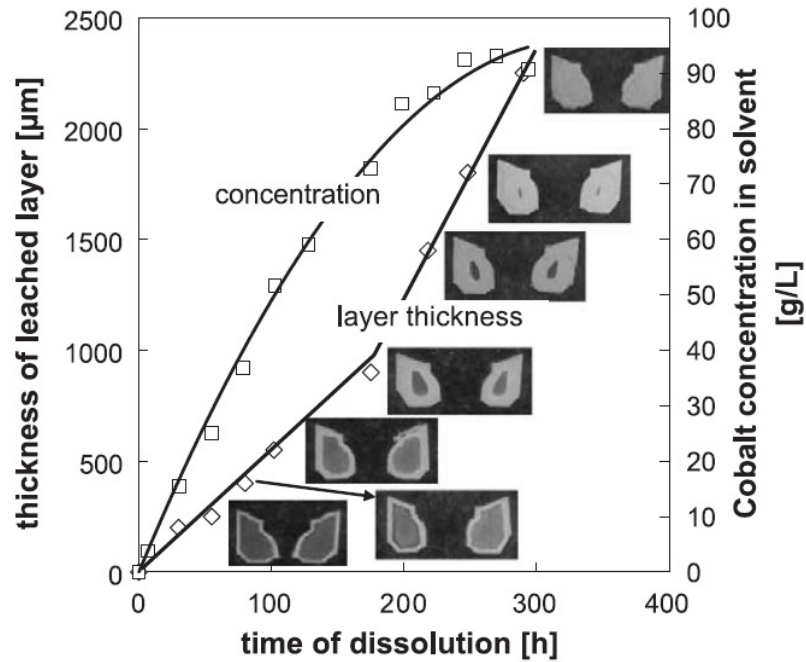


Figure 2-9 Extraction of Co as cobalt acetate and the progressive evolution of a leached layer in hardmetal scrap by contact with aqueous acetic acid (60°C) and simultaneous introduction (bubbling through) of oxygen (80L/hr) and 5.3M acetic acid solution [3].

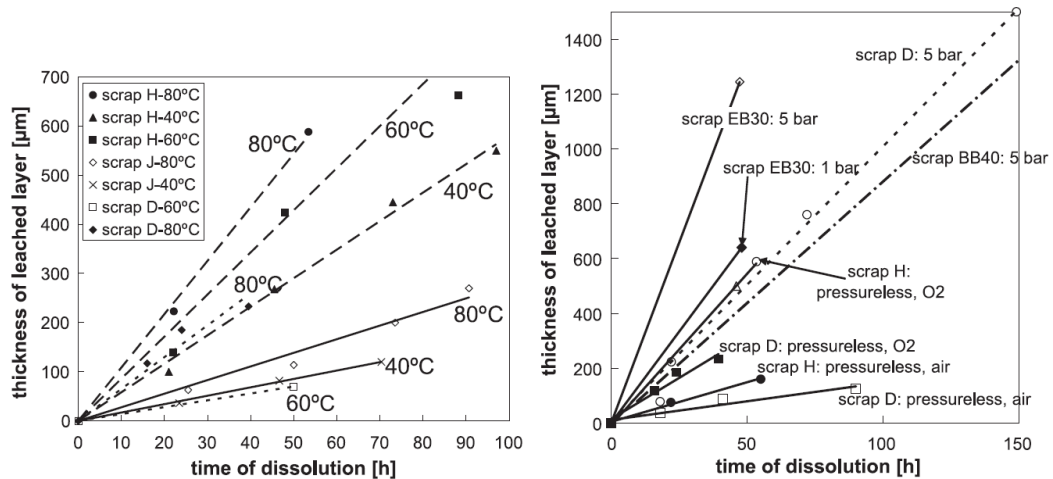


Figure 2-10 Left: graph showing the thickness of the depleted layer against time of dissolution at different temperatures with 25L/hr of oxygen throughput. Right: Thickness of the leached layer of different hardmetal scrap materials by contact with hot, aqueous acetic acid of 3.6M concentration and indicated pressures and atmospheres, at 80°C [3].

It was noted [3] that the finer the grain size and the more additive phases present e.g. TiC, TaC etc., the longer the dissolution time required. According to Edtmaier et al. [3] and Meissl [7], cobalt acetate solutions can be used for the recovery of cobalt as fine metallic powders which can subsequently serve as raw materials for new hardmetals manufacture.

2.3 Rheology

2.3.1 Introduction

Rheology is the science of the deformation and flow of matter. It is the study of the manner in which materials respond to an applied stress or strain [53, 54]. All materials have rheological properties and the study is relevant in many fields of study such as geology, concrete technology, soil mechanics, polymers, composites, tribology and many more in which the material behaves as a fluid. In powder metallurgy (as a directly relevant example) slurry rheology directly impacts the formation and properties of spray dried granules in terms of density, shape, morphology and particle size distribution of the dried powders [55, 56], which in turn impacts powder rheology.

Since rheology is the study of the deformation of matter, an understanding of stress and strain is necessary. Strain is simply defined as the change in length (δL) of an object compared to (divided by) its original length (L_o) in response to an applied force, to some new length 'L'. Figure 2-11 shows a rectangular bar undergoing strain, described by the equations:

$$\varepsilon = \frac{\delta L}{L_o} = \frac{L-L_o}{L} = \frac{L}{L_o} - 1 \quad (2)$$

or

$$\varepsilon = \int_{L_o}^L \frac{\delta L}{L} = \ln\left(\frac{L}{L_o}\right) \quad (3)$$

Where: equation 2 represents the Cauchy strain expression, mostly used for small strains and equation 3 is the Hencky strain, which is used for large deformations [53]. The choice of equation is largely a matter of convenience and are approximately equal at small strains.

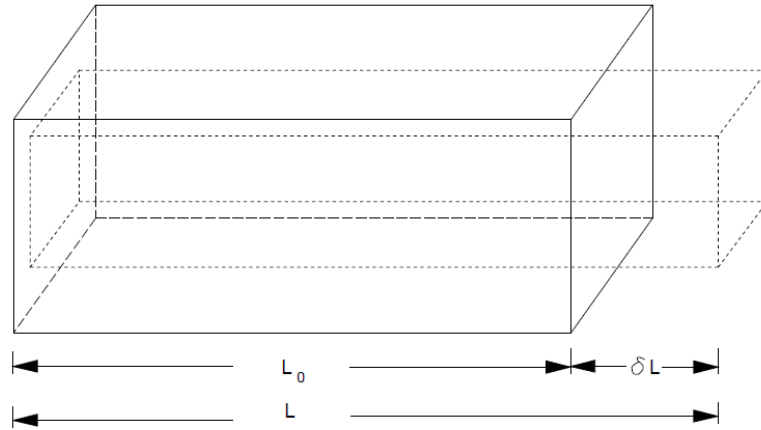


Figure 2-11 Linear extension of a rectangular bar [53].

Simple shear is fundamental to rheological studies and is illustrated in Figure 2-12. If a rectangular bar of height h is sheared, the upper plate of that bar is linearly displaced by an amount equal to δL . Each element of the bar is subject to the same level of deformation, hence the size of the element is not relevant [53]. The angle of shear is given by:

$$\tan \gamma = \frac{\delta L}{h} \quad (4)$$



Figure 2-12 Shear deformation of a rectangular bar [53].

Stress is defined as a force exerted per unit area and is usually expressed in Pascals, and can be tensile, compressive or shear. Equations that govern rheology and that show the relationship between stress and strain, are known as state or constitutive equations and include other variables such as temperature, pressure and time [53].

The study of stresses and strains in fluids is performed by subjecting them to a shear at a known rate. Ideally, this is performed using parallel or concentric plates with a fluid gap between them. One plate is fixed, while the other is moved at a known velocity. A force per unit area is required for motion, resulting in the shear stress (σ) required to move the plates through the fluid. Shear rate (also called strain rate) is defined as the velocity of the moving surface relative to the stationary surface, divided by the distance between the surfaces, and is measured in reciprocal seconds. Figure 2-13 shows the velocity profile of two parallel surfaces, where 'h' is the distance between the parallel plates and 'u' is the velocity of the top plate, while the bottom plate is held stationary. Most liquid and slurry rheometers use parallel or concentric surfaces (such as those in Figure 2-13) to determine the forces required to move the plates past one another, with the presence of the fluid to be studied between them, hence yielding information about the flow behavior of the medium. Powder rheometers use various different techniques (discussed further in a later section), but the underlying concepts are the same.

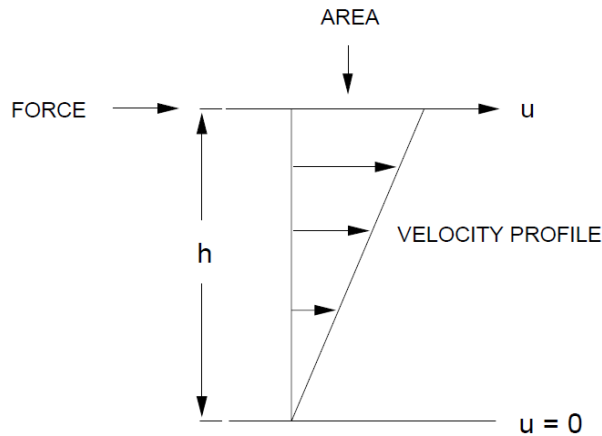


Figure 2-13 Velocity profile between parallel plates [53].

2.3.2 Slurry rheology

Slurry rheology testing is performed under laminar flow conditions, ensuring steady shear behavior. If this is not done, little useful information is gathered by attempting to measure turbulent flow. The shear rate can vary widely based on the application, for example, spray drying imparts very high shear conditions (10^3 - 10^5 s^{-1}) to the slurry, mixing or stirring imparts moderate shear conditions (10^1 - 10^3 s^{-1}) while sedimentation of particles typically occurs under very low rates of shear (10^{-6} - 10^{-3} s^{-1}) [53].

Viscosity (resistance to flow) is defined mathematically as the shear stress divided by the shear rate, and is usually reported in Poise (Pa.s) for high viscosities such as those of pastes or gels, or centipoise / millipascal seconds (mPas) for most everyday free flowing liquids.

Fluids can behave rheologically in a number of different ways when sheared, and this behavior is illustrated in Figure 2-14. Newtonian fluids, the simplest of all fluids, follow a linear behavior of shear stress against shear rate passing through the origin (hence even the smallest shear rate applied to such a fluid, produces a shear stress and particle flow, an example is water), while other time independent

fluids show different behavior based upon the rate of shear, examples include Herschel-Bulkley, Bingham, shear thickening and shear thinning, non-Newtonian behaviors [53, 57].

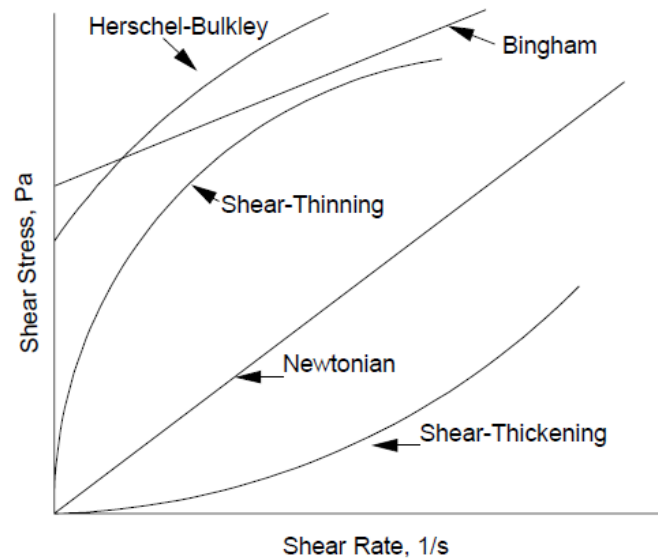


Figure 2-14 Typical time independent fluid rheology curves [53].

An important characteristic of Herschel-Bulkley and Bingham plastic fluids is the fact that they possess a yield stress, which is defined as the finite stress required to initiate flow [53], or the stress threshold below which no particle rearrangement can occur [54, 57].

In powder metallurgy, slurry rheology directly impacts the formation and properties of spray dried granules in terms of density, shape, morphology, and particle size distribution after spray drying. The properties of the spray dried granules directly impact the strength of the final sintered part [54-56]. For most ceramic systems, the ideal granules should be uniform, solid spheres [54]. The spray dried powder should be readily flowable to allow the powder to be compacted into a desired shape under applied pressure. The formation of spray dried granules and their dependence on slurry characteristics has been studied by Walker et al. [54] and Bertrand et al. [55]. The formation of granule shapes and structures were discussed by these authors in which elongated, donut shaped and

especially hollow granules were investigated. The most common problem associated with spray drying of ceramic or hardmetal slurries is the formation of a large internal void, leading to a hollow granule. During spray drying, granule formation occurs in a number of stages. Stage 1: atomization of the feed slurry into droplets, stage 2: deceleration of the droplets to the speed of the drying air that is circulated through the drying chamber, stage 3: droplet drying and finally stage 4: separation of the dried material from the airstream. In stage 1, when a droplet is formed in the spray drying nozzle under very high shear, a brief period is required for the droplet to reach thermal equilibrium with the drying atmosphere, during which very little drying occurs [54]. Drying of the droplet then proceeds at a constant rate, while the surface of the droplet is saturated with liquid. After a critical point, the drying rate decreases and the liquid-vapour interface recedes in a way referred to as a shrinking wet core. For slurries containing dissolved solids, the critical point occurs when the surface of the droplet forms a dry shell, if the particles still present within the wet core are not sufficiently in contact, to prevent further particle rearrangement, a hollow granule (possessing a large internal void) may result. If the internal temperature exceeds the boiling point of the liquid medium, the granule may even rupture [54]. Various further mechanisms for the formation of these hollows have been suggested including, ballooning (where internal pressure causes droplet expansion as vapour forms within the droplet with increasing temperature), a rapid moisture evaporation rate at a pace faster than the diffusion of solids back into the droplet interior, and liquid migration, causing solids to move to the surface of the drying granule under capillary forces, as well as entrapped air within the slurry creating porosity [55, 56].

The rheology of suspensions and slurries is complex and there is no single parameter that can be used to explain it [58, 59]. Factors influencing slurry rheology include grain size distribution and shape, solids loading (volume % solids), dispersant content, polymer binder addition, pH, zeta potential (charge effects) and temperature [58-63].

Zeta potential is a measure of the charge stability of a slurry. When a charged particle (including a closely bound layer of solvent) moves within a liquid environment, the zeta potential is defined as the potential difference between the slip plane and the bulk liquid, see Figure 2-15. Since like charged ions repel and unlike charges attract each other, the zeta potential measures the tendency of a slurry to agglomerate or remain dispersed [64]. A zeta potential close to zero indicates a tendency towards agglomeration, while a negative or positive potential indicates a more stable suspension [65].

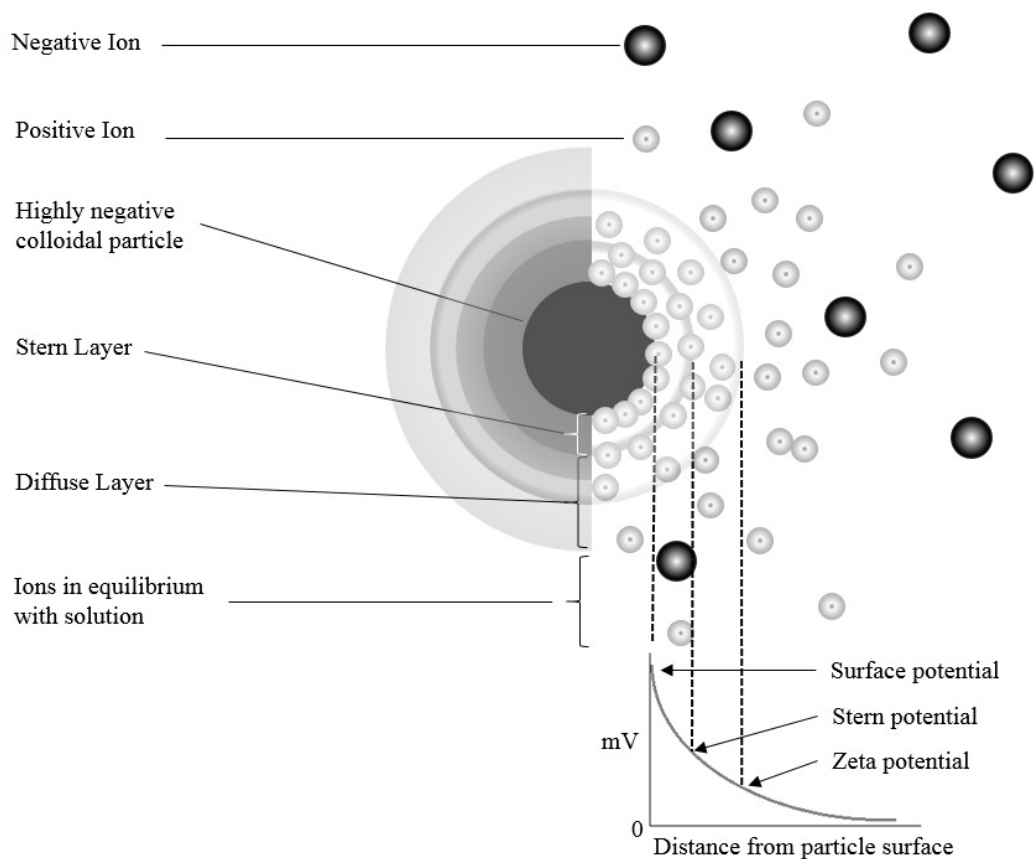


Figure 2-15 A charged colloidal particle in suspension. Zeta potential is given by the potential difference between the slip plane around the particle and the bulk solution.

An understanding of slurry rheology is required to produce ideal, dense granules when spray drying. Various models have been formulated to describe slurry

rheology mathematically, including the power law [65-67], Casson [65, 66, 68], Bingham plastic [58, 65, 66], Sisko [65, 66] and Herschel-Bulkley [65, 66] models. When the slurry yield stress is low, the powder particles can pack to a high density as the liquid phase is evaporated during spray drying, resulting in a thickened granule 'shell' and an internal void within the granule [54, 55]. Conversely, when the slurry yield stress is high, solid granules form [54, 55]. Hence the slurry yield stress directly impacts the granule microstructure and hence also the powder properties. Walker et al. [54] studied flocculated and deflocculated slurry rheology, and the impact of this on spray drying. Figure 2-16 shows the granule formation model for flocculated and deflocculated slurries. Flocculated slurries were those possessing a high yield stress because they contained less deflocculant: a dispersant or surface active agent (surfactant) that reduces surface tension and attractive forces between slurry particles. Flocculated slurries (or those possessing a high yield stress) produce solid granules, while deflocculated and freer flowing slurries tend to produce hollow granules, as shown in Figure 2-16. Figure 2-17 (a) and (b) show cross sectioned and polished granule microstructures of flocculated (high yield stress of approximately 100Pa) and deflocculated (low yield stress of approximately 0.1Pa) slurries respectively. The dense granules occurred in the case of slurries possessing a high yield stress [54].

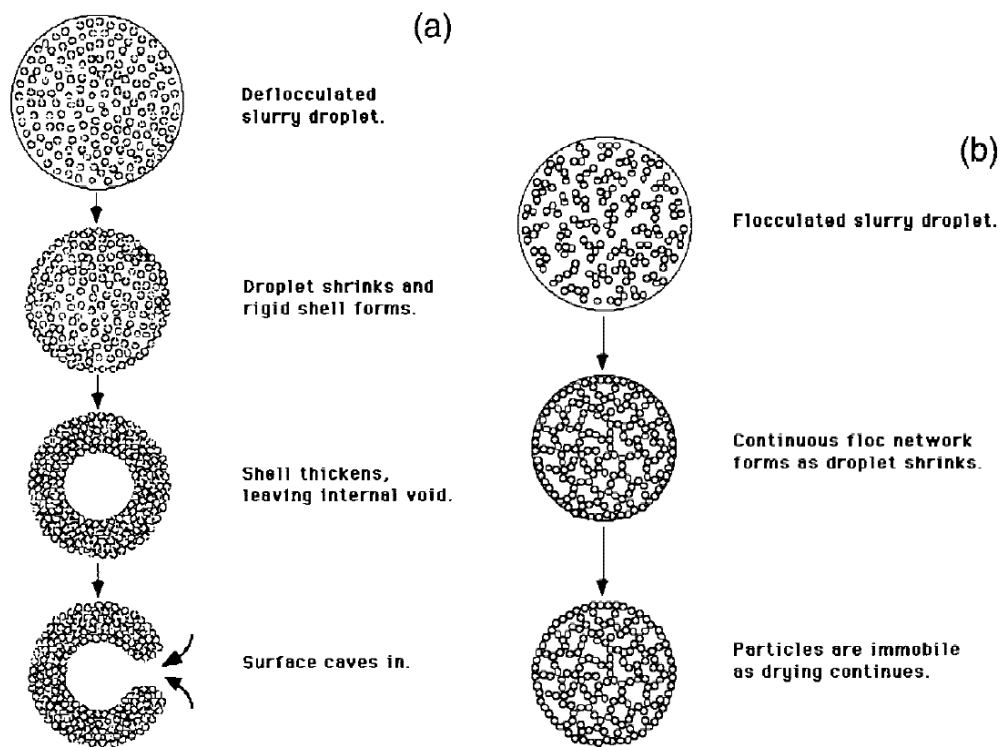


Figure 2-16 (a) Granule formation in deflocculated slurries. (b) Granule formation in a flocculated slurry [54].

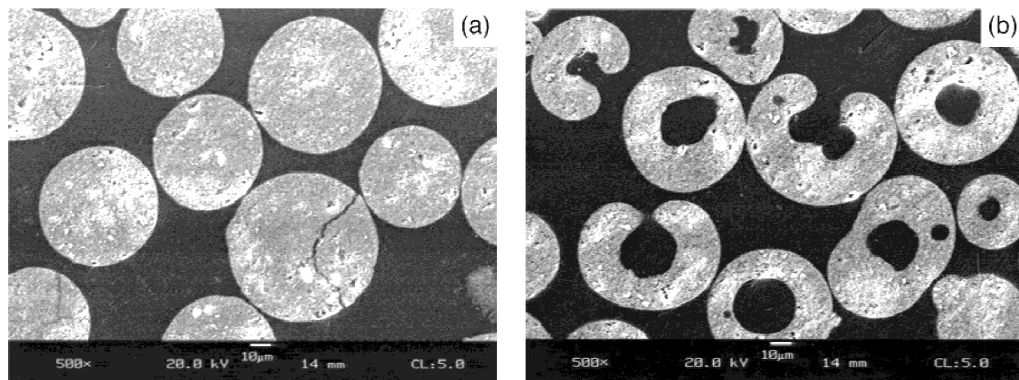


Figure 2-17 Polished sections of granules containing (a) 30vol.% solids, 0.35wt% deflocculant and (b) 40vol.% solids, 1.0wt% deflocculant.

Bertrand et al. [55] studied the influence of spray drying and slurry parameters on alumina powders, and agreed with the mechanisms proposed by Walker et al. [54]. The effects of varying amounts of organic additives, pH environment and zeta potential, were investigated [55]. The flow curves and yield stress results can be seen in Figure 2-18. The spray dried alumina powders are shown in Figure 2-19 and 2-20.

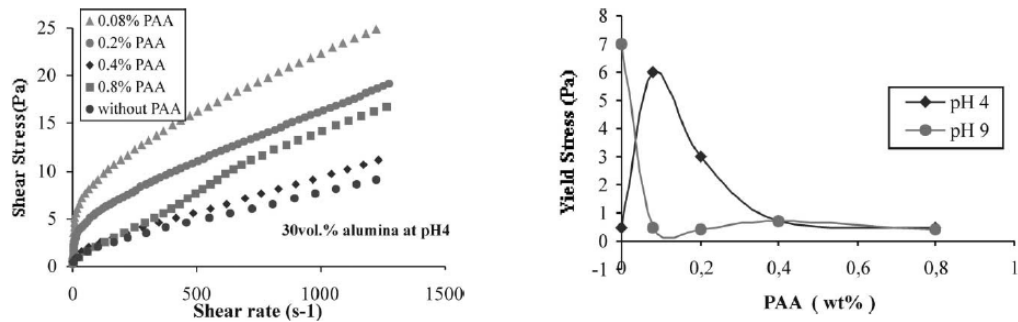


Figure 2-18 Left: Flow curves for 30vol.% slurries as a function of PAA (ammonium polyacrylate dispersant) concentration. Right: Variation in the Casson yield stress value, calculated using the Casson model, at pH 4 and pH 9 [55].

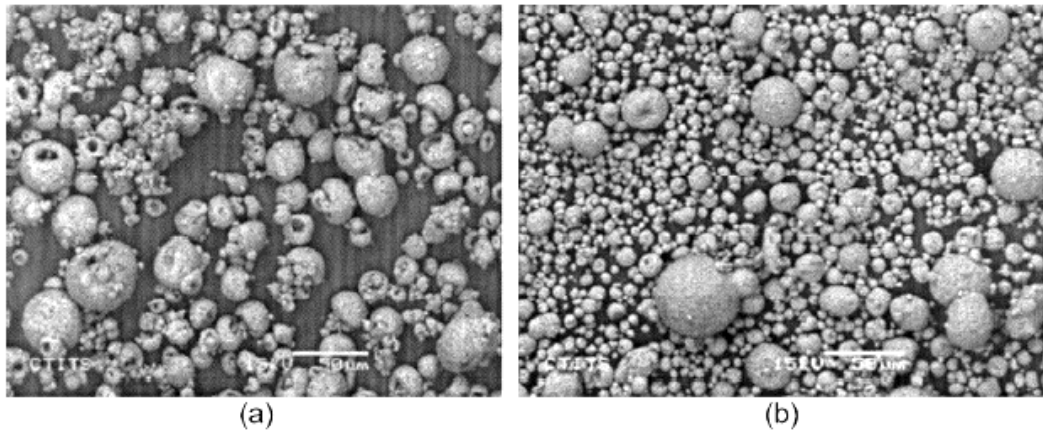


Figure 2-19 Alumina granules studied by Bertrand et al. [55]. (a) 0.08% deflocculant, 15% binder, pH of 9. (b) 0.08% deflocculant, 15% binder, pH 4.

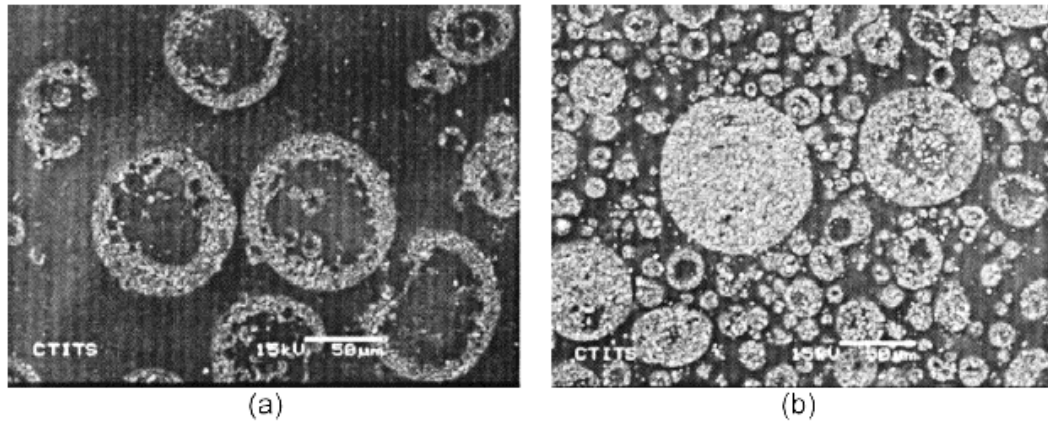


Figure 2-20 Polished cross sections of the alumina granules in Figure 2-13 [55].

Hollow granules resulted from higher dispersant levels ($> 0.08\text{wt}\%$ PAA), because of the lower viscosities and shear stresses for these slurries, as can be seen in Figure 2-18. The highest yield stress corresponded to the $0.08\text{wt}\%$ dispersed slurry, at a pH of 4, which yielded solid granules: proving that charge environment and zeta potential can play a major role in slurry rheology and ultimately spray dried granule structure and formation. The tapped density and flow rate of the powders was also measured, and it was found that the dense granules produced free flowing powders and the highest tapped density [55]. From the above results, it can be seen that powder rheology is directly affected by the properties of the precursor slurry, and there is a high degree of overlap between the study of slurry rheology and powder rheology. Powder rheology, though similar in principle to slurry rheology, requires different technologies and techniques to be characterized, which is discussed in the following section.

2.3.3 Powder rheology

Spray dried powders are usually pressed into a ‘green’ compact, and sintered into a final, dense part. An advantage of this method is rapid production and ease of automation. Parts manufactured from spray dried powders can, however, experience various strength limiting defects because of the granule characteristics and microstructure as well as powder flow behaviour during compaction [54].

Hence, the capability of manufacturing complex geometries is limited by the quality of the spray dried powders and the flowability and pressability of these powders.

The flow of powder is dependent on a large number of factors [69]. Leturia et al. [70] classified powder behaviour into three major categories. The first category refers to a powder's intrinsic properties (found in each particle) for example roughness, individual particle size, shape, porosity and density. Bulk properties of the powder bed comprise the second category, including factors such as the overall bulk particle size distribution, cohesion, bulk density and frictional interactions. The third category refers to external factors influencing powder behaviour, including temperature, humidity, voidage and degree of compaction [70]. In addition to these, Madariaga et al. [71] has discussed the effects of interparticle forces such as Van Der Waal's, electrostatic and capillary forces on powders, highlighting even more variables contributing to powder flow.

McDougall et al. [72] stated that the outflow of powder from a hopper is influenced by the air pressure and pressure of the powder at the outlet, while Freeman et al. [73] stated that air content in a powder bed is arguably the most important of many factors influencing powder rheology. From these various perspectives, it is clear that powders are complex materials, requiring a range of methods to provide sufficient understanding of their flow behaviour [69, 70, 72, 74]. There is no single, ideal way of measuring and characterizing these complex materials [75], because unlike solids, granular materials conform to the container shape, can possess shear stresses in the absence of a deformation, possess a critical stress of shear depending on the applied normal stress [76] and are fundamentally heterogeneous materials [77]. Many powders are cohesive to some degree and the understanding of their flow behaviour is fundamental to many manufacturing processes [78]. Poor flow of powders leads to downtime, wastage and maintenance problems [70].

Commercially available rheometers have been shown to be suitable for distinguishing differences between powder preparation methods, particle packing and bulk behaviour [74]. Rheometers are capable of distinguishing different powder samples from one another, are good for quality control purposes and are sensitive to particle packing and preparation differences between powders [74] and certain rheometers are fast, repeatable and accurate [75]. However, a given mass of powder can contain varying amounts of air [73] and powder rheology is very sensitive to the spatial arrangement of the granules [71], as well as the many other factors described earlier, therefore most rheometers do not give a complete understanding of each powder, again reinforcing the need to perform a wide range of powder tests to understand particulate materials.

The FT4 powder rheometer, developed by Freeman Technologies in the United Kingdom, has become a widely used commercial rheometer that can measure a wide variety of powder properties. The original designer of the rheometer, R.E. Freeman, based the operation of the rheometer on the blade and shear cell designs shown in Figure 2-21. The downward action of the blade generates a compressive, bulldozing action onto the powder bed, while the upward motion generates a lifting and shearing action [75]. The shear cell uses multiple slots to slowly shear one plane of powder over another, hence measuring the shear response of the powder bed. The rheometer is capable of other measurements and techniques, but the shear and flow data generated by the shear cell and rheometer blade are the most well documented methods in literature. Freeman et al. [69, 73, 75] have demonstrated some potential applications of the rheometer with the analysis of various different powders such as lactose of various morphologies and sizes, talcum, limestone, and ceramic powders. Other authors have used the rheometer to study various materials such as PVC and carbon powders [70], as well as spherical and irregular glass beads in order to model the flow properties of powder particles [74].

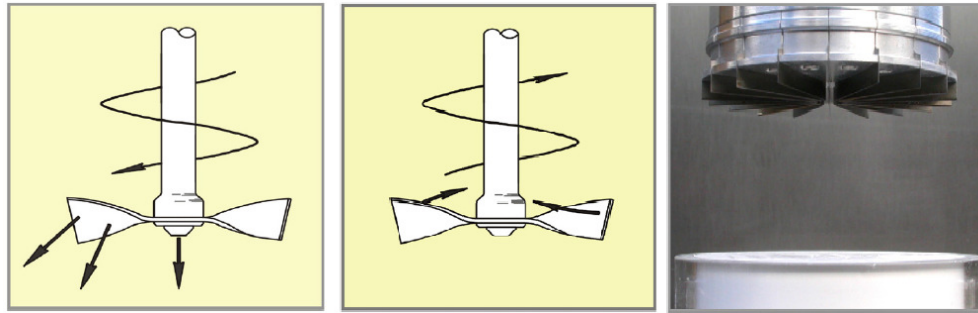


Figure 2-21 A: Downward testing mode showing bulldozing action along the entire blade length, B: shearing and lifting with minimal consolidation, C: shear cell preparing to enter the sample vessel [75].

The powders tested by Freeman also accounted for different particle shapes and sizes, ranging from 4 to 130 μ m in size, and comprising spheres, angular shapes and even platelet shaped particles, and a range of powder densities from 0.46 to 0.76g/ml. The flow properties of various powders measured by Freeman are shown in Figure 2-22. Each powder achieved a distinct flow energy measured in mJ, allowing the rheometer to distinguish differences between the powders, such as spray dried lactose, sieved lactose and coarsely and finely milled lactose.

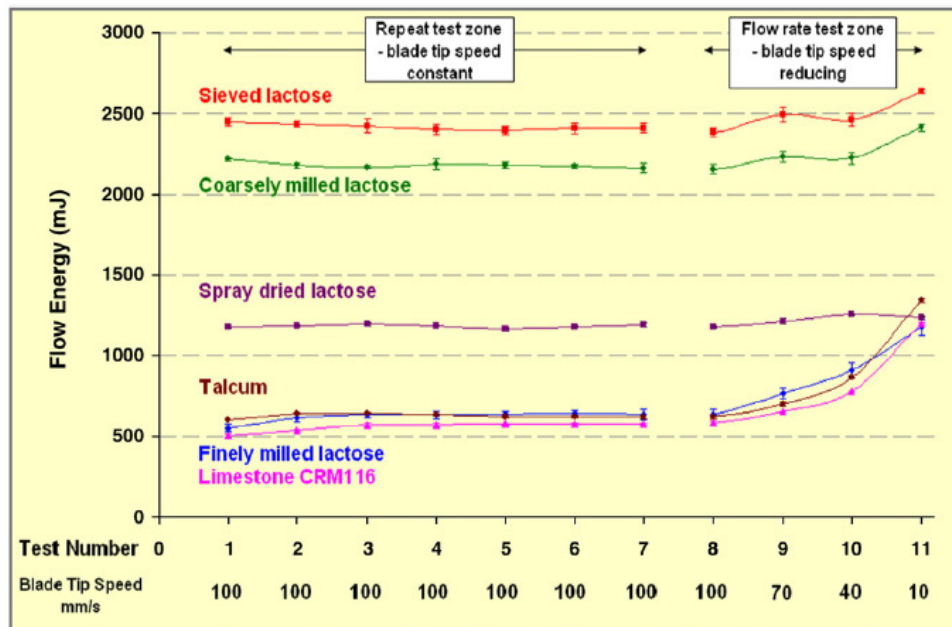


Figure 2-22 Flow energy measurements at fixed and variable blade speeds [75].

Shear results for the various powders measured by Freeman [75] have been shown in Figure 2-23. The rheometer was able to distinguish differences between the shear behaviour of the different powders, however the authors noted that the accuracy of the shear data was high (reproducibility within 1%) in the case of the non-cohesive powders, but became inaccurate in the case of cohesive powders and is not suitable to reliably distinguish between very similar powders, where conversely the simple flowability (flow energy) measurements are highly suitable at differentiating even very similar powders from each other. The authors state that the shear analysis technique requires further development because of the generated pressures ahead of the shear mechanism's motion and the shear strength and compressibility of the material, making it more difficult to distinguish the results of the shear analysis clearly in each case [75].

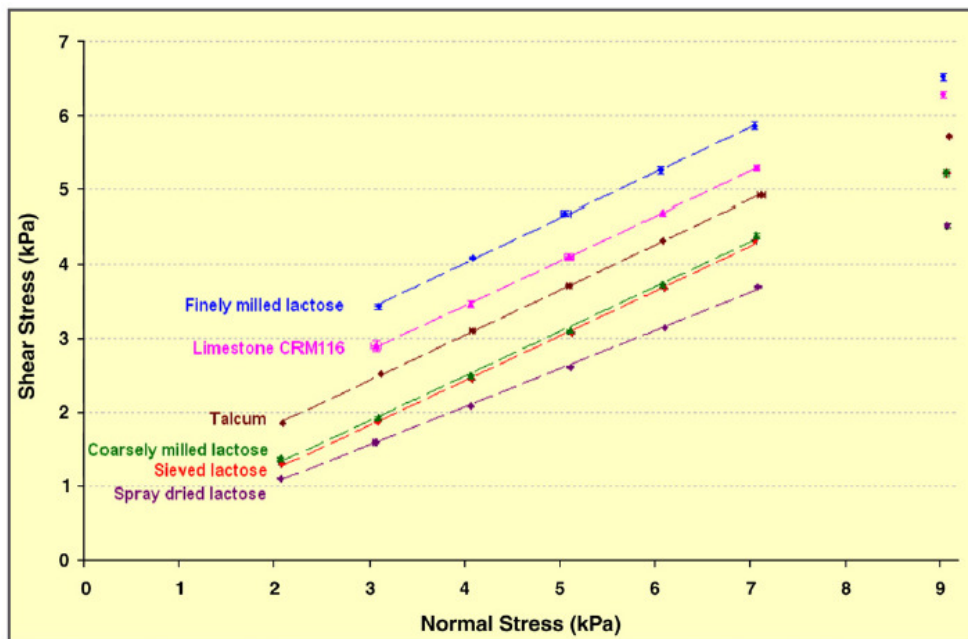


Figure 2-23 Shear test yield loci for 6 materials following pre-shear at 9kPa normal stress [75].

Compressibility, and aeration response of the powders are other techniques that can gather useful data about powders using the FT4 powder rheometer. The same powders (shown above) studied by Freeman [75] are shown in Figures 2-24 to 2-26. The various powders responded very differently to compressibility, as shown

in Figure 2-24 (measured using a vented piston assembly) with the finest or most cohesive powders compressing the most, and coarser particles compressing the least. Freeman observed that compressibility can be a very useful technique for differentiating powders.

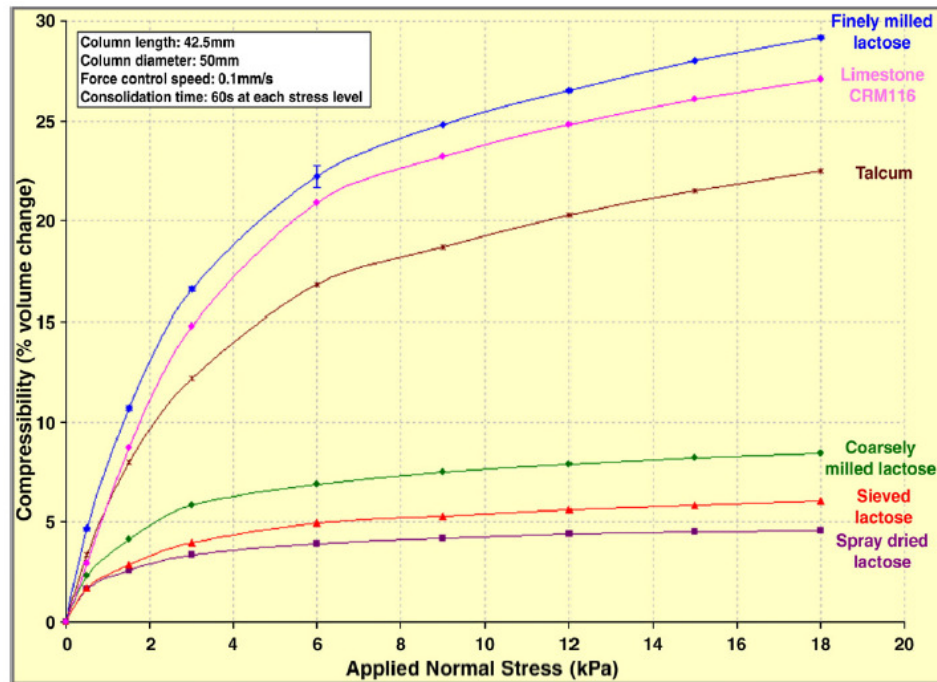


Figure 2-24 Bulk compression of initially conditioned samples as a function of applied normal stress [75].

The powders subjected to aeration testing (Figures 2-25 and 2-26) were clearly distinguishable, with the powders experiencing a change in flow energy in response to aeration and fluidization (Figure 2-25), and the ease with which the powder bed releases air from its bulk (Figure 2-26).

In the words of Leturia et al. [70]: “Powders and bulk materials cannot be viewed as invariant entities and their flow properties cannot be predicted by any one indicator. The connection of several characterization methods is required to ensure a complete understanding of the powder flow properties over a wide range of conditions. This approach allows better insight into the powder/process relationship.”

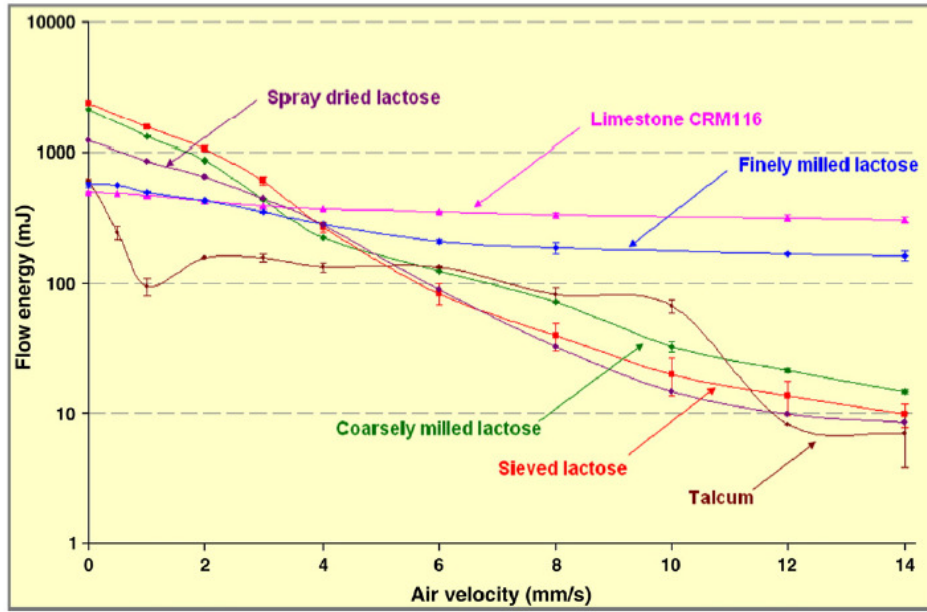


Figure 2-25 Flow energy (log scale) as a function of air velocity [75].

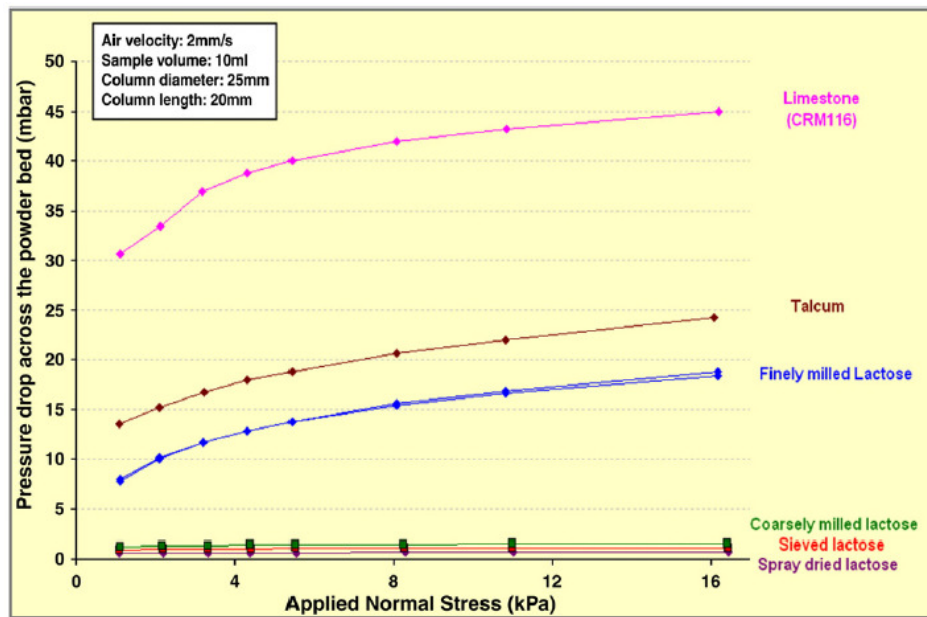


Figure 2-26 Pressure drop across the powder bed at 2mm/s air velocity as a function of applied normal stress [75].

3. EXPERIMENTAL PROCEDURE

3.1 Introduction

Three classes of WC-6wt% Co materials were studied in this work, namely new (also commonly referred as ‘virgin’ material), zinc recycled and acetic acid recycled materials. In this study, bulk quantities were produced in two mill sizes: 80 litre mills and 600 litre mills: referred to as ‘laboratory’ and ‘industrial’ mills respectively. Although the ‘laboratory’ mills still produce large quantities (50kg to 120kg), they are referred to as ‘laboratory’ mills because they were operated independently of the production process at Pilot Tools (Pty) Ltd, under controlled conditions.

The new and zinc recycled materials were studied under both laboratory and industrial milling conditions, in order to provide a broader basis for comparison. The acetic acid material was produced under laboratory milling conditions, and then compared to the new and zinc recycled materials. Currently, full scale industrial production of acetic acid recycled materials is not done.

The experimental procedure begins by explaining the material history of each class of powder studied in this work i.e. new, zinc recycled and acetic acid recycled powders. After which the general manufacturing processes, to which the powders were subjected, are explained. The different techniques used to study and characterize the materials are also described.

3.2 Materials and recycling methods

3.2.1 New powders

Tungsten carbide 4.0µm powder sourced from Metal-Tech Ltd and cobalt powder sourced from Shu Powders Africa, were used to provide the starting material for production of the new (virgin) WC-6wt% Co materials.

3.2.2 Zinc recycling

Graphite crucibles containing pure zinc and used cemented carbide components, (mining tool scrap) and a single crucible containing 100kg of sintered laboratory milled material, were included in a standard industrial PRZ run at Pilot Tools (Pty) Ltd. The total furnace load was 1100kg. The furnace was then evacuated of air and filled with argon. The weight ratio of zinc to binder metal is typically in the range of 10:1 to 30:1 [4]. A weight ratio in this range generally allows for successful zinc penetration of the scrap if the hold-time at the infiltration temperatures is sufficient [4]. The temperature of the furnace was raised to 930°C and held for 24 hours to allow for zinc infiltration. Typically a temperature greater than 750°C is suitable for this process to work [4] and can vary between recycling plants. Removal of the zinc was accomplished by a powerful vacuum and distillation process at 960°C, over a 36 hour time period, after which the load was gradually cooled to room temperature. When components larger than 15mm in diameter are recycled, partially zinc attacked by-product material can result, which is then referred to as ‘oversize material’.

In the current study oversize samples (~20mm diameter) were extracted from the recycled product, metallographically prepared and then characterized using several complimentary techniques described in detail later. The oversize samples were analysed in order to determine its origins and implications for recycling.

Furthermore, the oversize material was used as the starting material for the acetic acid recycling process; reasons provided in the next section.

3.2.3 Acetic acid recycling

Zinc recycled oversize material was used as the starting material for the acetic acid recycling process. As partially zinc attacked and porous material, the oversize material represented the best possible scenario for the acetic acid recycling process, without the need to use a complex pressure vessel and / or pure (and expensive) oxygenation of the acetic acid. Edtmaier et al. [3, 6] showed that the acetic acid leaching process is time intensive. Hence in this work, the acetic acid recycling process was investigated as a simple and environmentally friendly supplement to the zinc recycling process, which could be used to reduce the oversize material into useable powder without incurring the cost of a second zinc recycling run (typically used on oversize material).

An acetic acid recycling plant, capable of leaching approximately 150kg of WC-Co material at a time, was designed and constructed in this project. A schematic of the plant is shown in Figure 3-1. This small scale design would allow the concept and the impact of using this method, on the quality of the resulting cemented carbide material, to be investigated. The plant was designed to operate at atmospheric pressure and 80°C with an air flow rate of 120 litres per minute. The air flow was achieved using a simple aerator system and Teflon (polytetrafluoroethylene) based bubble stones placed at the bottom of the tank. A Teflon support platform was manufactured, in order to support the cemented carbide scrap above the heating element and bubble stones, while allowing for the bubbles to pass through it and to infiltrate the scrap volume. The temperature was controlled using a thermostat connected to a thermocouple, and was maintained to within 2°C margin of error (the deviation was due to the large size of the bath i.e. 750mm high and 400mm wide).

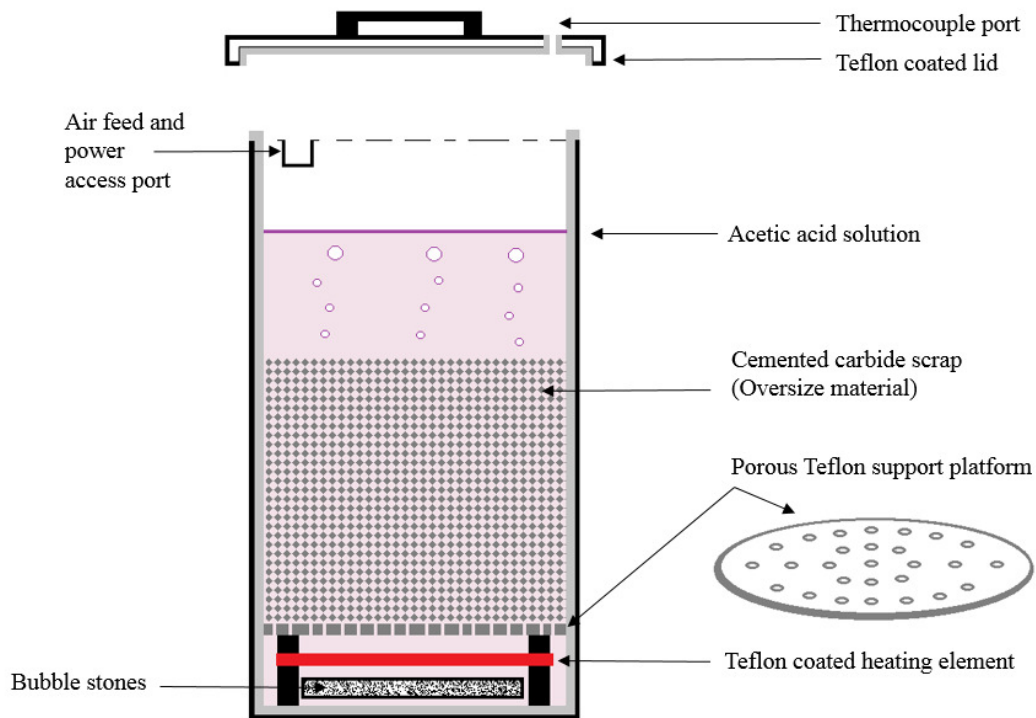


Figure 3-1 *Acetic acid recycling plant.*

The pH of the acetic acid plant was measured at regular intervals using a Mettler Toledo, SevenGo portable pH meter. The initial acetic acid mixture was produced to create a pH of 1.85, and when the pH increased above a value of 3, and the dissolution rate (pH rate of change) slowed significantly, additional acetic acid was added to the plant. The goal was to keep the pH below 4 at all times to maintain cobalt extraction, in accordance with the work of Edtmaier et al. [3]. The plant was run for 21 days, with the progress of the leaching process tracked by monitoring the depth of the cobalt depleted layer with time. After the test the acetic acid was extracted, and the material washed with water repeatedly until the purple hue of the cobalt acetate was removed, and the material was clean. Samples of sintered, new (i.e. virgin) materials were immersed in the acetic acid for comparison to the oversize material. The leached scrap was then dried, and crushed (homogenized) in an 80 litre ball mill with ethanol into powder form and then analysed for chemical purity and composition using inductively coupled plasma optical emission spectrometry (ICP-OES, described later). The dried

acetic acid leached powder was used to produce WC-6wt% Co material for comparison with the new and zinc recycled laboratory milled materials.

3.3 Milling

Three types of mills were used during the course of this research. The large production mills and laboratory mills (of capacity 600 litres and 80 litres respectively made from stainless steel) were used to manufacture the bulk quantities of the powders. Benchtop mills (capacity 2l and lined with WC, thereby preventing contamination from mill wear products) were used to prepare small slurry quantities for rheological analysis as well as to compare the milling behaviour of the new and recycled powders. A 3:1 ratio of cemented carbide milling media to powder load was used in all milling performed in this work. Table 2 on page 49, summarizes the slurries and powders produced for this study which are described in the following sections.

Production size powder batches of 888kg were produced under typical production conditions at Pilot Tools (Pty) Ltd. This production material is referred to as NP-prod (new powder, production milled) and PRZ-prod (zinc recycled, production milled) in this thesis. The PRZ-prod (zinc recycled, production milled) powder batches were produced from zinc recycled mining components blended with new powder. Typically, 60 to 70wt% PRZ material is blended with new material at Pilot Tools. The reason for the dilution is that recycled mining scrap typically possesses greater than 6wt% Co (usually 8 to 12wt% Co on average), thus requiring blending, to return the batch stoichiometry to 6wt% Co. NP-Prod and PRZ-Prod powder batches were milled in 13.65wt% ethanol. Polyethylene glycol polymer binder was added 4 hours before the end of the mill cycle. After spray drying each powder, 50kg was removed for further testing and analysis.

100 kg of new WC and 6wt% Co powder was milled in the 80 litre (laboratory) mills in ethanol. This powder is designated NP-lab (new powder, laboratory

milled) in this thesis. The initial 100 kg of NP-lab powder was spray dried, pressed into cylinders, sintered and then recycled using the zinc process. This recycled product was crushed and dry-milled back into powder form and 50kg was used to produce the powder designated in this research as PRZ-lab (zinc recycled, laboratory milled) powder. A further 50kg load of NP-lab powder was milled and spray dried for the powder and slurry characterization tests, and to provide NP-lab material for comparisons with the recycled materials. AC-lab (acetic acid recycled, laboratory milled) was produced from leached oversize material from the acetic acid plant, with some new cobalt added to bring the batch composition back to 6wt% Co. When milling the laboratory milled powders, polyethylene glycol (binder) and dispersant were added at the beginning of the mill cycle and 16.67wt% ethanol was used to achieve an adequate (> 70%) granulated spray dried powder yield.

In order to determine the impact of grain size variation on the properties of the slurry and the granulate, a new batch of NP-prod powder was milled to a coarser size (approximately 2.0 μ m) using the same slurry conditions (13.65wt% alcohol) and 3:1 milling ratio as for a production batch, but utilizing a 100kg load in a laboratory mill. This powder is designated NP-prod-remill.

Small batches of WC-6wt% Co were also milled in the 2 litre benchtop mills in order to measure the influence of a broad grain size range on slurry rheology (discussed later). Milling curves were generated using the small 2 litre benchtop mills. Test batches of NP, PRZ and AC materials were milled to compare the milling behavior of all three WC-6wt% Co materials directly, under identical conditions. Milling was performed for 28 hours, with samples extracted at two hour intervals during the first 8 hours, and then every four hours until milling was completed.

All powder particle sizes were analyzed using a Microtrac S3500 particle size analyzer, and some samples were dried for SEM analysis. The mean volume (Mv)

grain size range of all the powders was 1.6 to 2.0 μm , with a target average grain size of 1.8 μm .

Table 2: Summary of the bulk slurries and powders produced.

Batch name	Alcohol (wt%)	Description of powder
NP-lab	16.67; 11.89	New powder, lab milled
PRZ-lab	16.67, 11.89	100% zinc recycled NP-lab powder, lab milled
AC-lab	16.67, 11.89	Acetic acid leached PRZ oversize material, lab milled
NP-prod	13.65, 11.89	New powder, production milled
PRZ-prod	13.65, 11.89	Zinc recycled mining scrap powder + new powder - blended, production milled
NP-prod-remill	13.65	Same milling procedure as NP-prod but milled in lab mill to 2.0 μm (coarser than before)
WC-1.3 μm	11.89	New powders used to test grain size effects on slurry rheology, produced in the benchtop mills
WC-1.4 μm	11.89	
WC-2.0 μm	11.89	
WC-2.9 μm	11.89	
WC-4.1 μm	11.89	
NP	16.67	Milling rate comparison, produced in the benchtop mills
PRZ	16.67	
AC	16.67	

3.4 Slurry rheology

Slurry rheology is one of the most important aspects of quality control when producing spray dried powders, which are central to powder metallurgy techniques. The various aspects of slurry rheology testing are covered in this section, beginning with polymer effects and followed by zeta potential, after which the apparatus and measurements are described. Table 2 summarizes all slurries studied in this work.

3.4.1 Polymer content and integrity

Because the various powders required different milling durations to achieve the target grain size, an investigation into the polymer integrity was conducted, to identify whether or not the polyethylene glycol molecules broke down during milling, thereby potentially influencing the slurry rheology results.

A mass fraction of 2.0wt% polyethylene glycol and 0.18wt% dispersant (a suitable, but proprietary, polysaccharide derivative) were used in this study. Gel permeation chromatography (GPC) was performed on the polymers extracted from the NP-lab, PRZ-lab, NP-prod and PRZ-prod powders. This would assess if a drop in molecular weight had occurred, which would indicate polymer breakdown, and in turn would affect the slurry rheology. A Waters 2414 Differential Refractometer was used at 30°C in series with a Waters 2487 dual wavelength absorbance UV/Vis detector operating at variable wavelengths. Tetrahydrofuran (THF, HPLC grade, stabilized with 0.125% BHT) was used as the eluent at flow rates of 1 mL/min. The column oven was kept at 30°C and the injection volume was 100µL. Two Polymer Laboratories (PLgel) 5µm mixed-C (300 x 7.5mm) columns and a pre-column (PLgel 5µm Guard, 50 x 7.5mm) were used. Calibration was done using narrow polystyrene standards ranging from 580 to 2x 10⁶g/mol. All molecular weights were reported as polystyrene equivalents. Samples were dissolved in BHT stabilized THF (2mg/mL). Sample solutions were filtered via syringe, through 0.45µm regenerated cellulose filters prior to analysis.

3.4.2 Zeta potential

The charge behaviour of the slurry particles can directly influence slurry rheology; hence zeta potential measurements were conducted to identify the dispersion properties of each slurry.

Powder samples (0.015g each) were dispersed for 30s in 10g of ethanol, using a Sonics Vibracell CV18 ultrasonic probe (130W, 20kHz), after which the samples were tested for zeta potential using a Malvern Nano-ZS zetasizer. Samples of all the slurries were tested in this way. Each sample was tested at 25°C and a pH of 7.3 (the pH value of pure ethanol).

3.4.3 Rheological preparation and measurements

To eliminate the effect of a possible change in the polymers when performing the slurry rheology tests, samples of each powder were subjected to a binder burnout step, to remove the polymers, in a vacuum furnace at 450°C for 1h. The binder-less powders then had fresh polymers re-introduced before slurry rheology testing commenced. WC-lined 2 litre mills were used to re-introduce the polymer to each powder, by milling for 3 hours. The advantages of using these mills were that no new wear products were introduced into the slurry (due to the WC lining of the mill), and the slurry was intimately homogenized prior to rheological measurements. To determine the effects of recycling on slurry rheology in more detail, thicker (more viscous) samples were also milled using a high solids loading condition of 11.89wt% alcohol. In addition, batches of new powder slurries were produced to determine the effects of grain size distribution on slurry rheology and zeta potential. These new powders were milled using new WC powder of different initial grain sizes ranging from 0.8µm to 8µm, each blended with 6wt% Co. The powders were milled to the final (measured) WC grain sizes indicated in Table 2 (p 49), which also summarizes the different alcohol wt% used for each slurry.

Slurry rheology tests were performed using a Brookfield R/S Plus Rheometer equipped with a Pt-100 thermocouple and temperature control jacket regulated by a Lauda Eco RE-420 temperature control bath. A CC40 co-axial cylinder spindle geometry was used for all experiments. A schematic of the operation of the rotational cylinder rheometer is shown in Figure 3-2. The temperature of the slurry was held constant at 25°C and the slurries were allowed to equilibrate to

temperature, while being gently agitated using an IKA Eurostar 40 digital mixer, equipped with a non-bubble generating turbine, inside a temperature control bath. After 5 minutes of agitation, 71ml of sample was extracted from the mixing cup and rheologically tested. Shear stress as a function of shear rate was measured over 120s, during which the spindle accelerates from 1s^{-1} to 500s^{-1} during the first 60s, and then decelerates to zero, at the same rate, in the final 60s. Settling tests were performed by rotating the spindle of the rheometer at a shear rate of 65s^{-1} for 30min, in which a variation in viscosity indicates sedimentation of the slurry over time [79].

Using the plot of shear stress against shear rate, approximate yield stress values were extrapolated from the y-intercept of the straight line graphs of the spray dried slurries, as for the Bingham plastic method [68, 80].

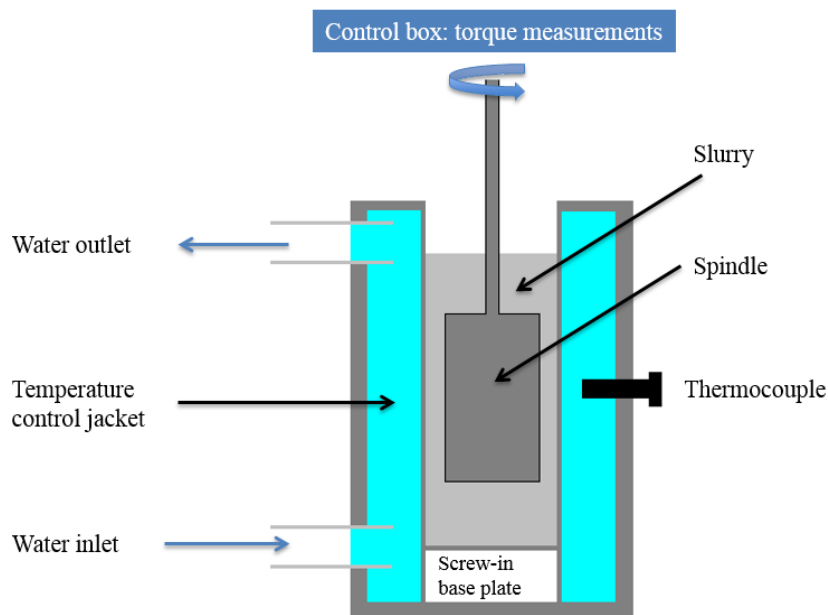


Figure 3-2 Schematic of a rotational cylinder slurry rheometer.

3.5 Powder preparation and analysis

3.5.1 Spray drying

Spray drying was performed at a constant 7 bar pressure using a Niro HC 120 mixed flow spray drier; identical nozzles and settings were used for each powder batch. The slurry temperature was held constant at 25°C by a slurry holding tank temperature control jacket.

3.5.2 Granule size and simple powder characterization

Powders were screened into discrete size fractions using 45, 63, 90, 125, 150, 180 and 212 micrometre screens, in a mechanical screen shaker system. A Turbotrac dry powder feeder, attached to the Microtrac S3500 particle size analyser, was used to measure the particle size distribution of each size fraction. Based upon ASTM standards [81, 82], apparent density and flow rate of the powders were measured. A Hall flow meter, using 100g of powder for each measurement, was used to measure the flow rate of each screen fraction. Apparent density was calculated using a 25mL vessel, containing powder of each size range, by measuring the mass and dividing by the known volume (25mL) of powder. Measurements were performed at least three times per screen fraction. Powders were micrographed at low magnification (in order to view the bulk powder appearance, granule surfaces, size distribution and packing arrangements) using an Olympus SZ-X16 stereo optical microscope with an SC30 digital camera and AnalySIS 5.2 software at 40X magnification for granules larger than 90µm, and 80X for finer granules.

3.5.3 Powder polishing

Powder granules were embedded in a copper containing thermosetting resin (to allow for beam conduction to facilitate SEM and micro-PIXE analysis) and were carefully polished in stages of decreasing diamond grit size, with a final polishing stage size of 1 micron. The samples were polished to reveal any internal voids within the granules (if present). A suitable granule with an exposed internal void was selected for analysis using optical microscopy. To ensure that ion beam range during micro-PIXE analysis did not exceed the localized depth of the cross section of a sphere, the beam was scanned over the walls of the cross sectioned granule, see Figure 3-3, which illustrates the polishing process. Under-polishing (Figure 3-3 A) could result in an occluded void beneath the analysis area, introducing errors due to the proton beam depth penetration, similarly an over polished sample - which could result in the resin beneath it being sampled by the beam (Figure 3-3 C).

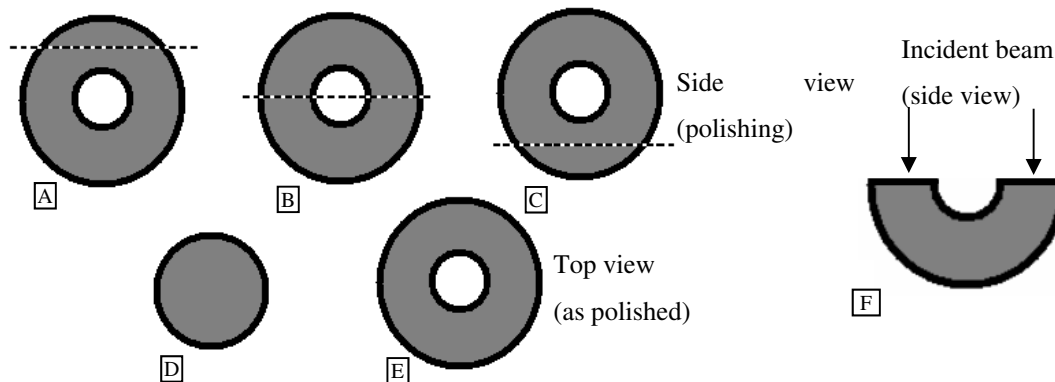


Figure 3-3 Graphical representation of the granule polishing process. The dotted lines indicate the point of polishing termination. A and C: under and over polishing respectively, result in a granule appearing solid as viewed from above (D), potentially still possessing a hidden void, or insufficient powder depth, unsuitable for proton beam analysis. B: polishing into an internal void ensures the required cross sectioned granule is exposed, for suitable analysis (E and F).

3.6 Powder rheology

An FT4 powder rheometer manufactured by Freeman Technologies Ltd was used to perform detailed powder rheology on the spray dried powders of the size ranges: 45-63 μ m, 90-125 μ m and 150-180 μ m for NP-prod, PRZ-prod, NP-lab, PRZ-lab and AC-lab. These discreet screen fractions were analysed, rather than the overall as-produced spray dried powders, in an attempt to minimize the dominant effects of particle size on the rheological properties, and rather focus on the materials related properties of the powders, such as the effects of recycling and humidity. Powder rheology tests were also performed on the humidified 45-63 μ m size fraction of NP-lab and PRZ-lab powders to compare 100% new against 100% zinc recycled powders in humid environments, and to verify the FT4 powder rheometer's sensitivity to spray dried cemented carbide powders. This was necessary because powder rheology is a relatively new and developing field of study and to the author's knowledge, no literature of cemented carbide powder rheology exists. The humidified powders were exposed to 75% relative humidity in a humidity chamber for 24 hours.

The set-up used in these experiments corresponds to the standard 48mm blade and 50mm diameter test vessels and equipment that were provided with the rheometer. Extensive descriptions and discussions for each test method employed by the FT4 powder rheometer are described elsewhere [75], however the specifics of each test method and the parameters used in this work are described below. Each experiment was performed three times, with the average results and associated errors, presented in this thesis. The blade testing mechanisms used by the FT4 powder rheometer are shown in Figure 3-4. The split vessel assemblies (used to exactly split a known powder volume and remove excess powder) are shown in Figure 3-5.

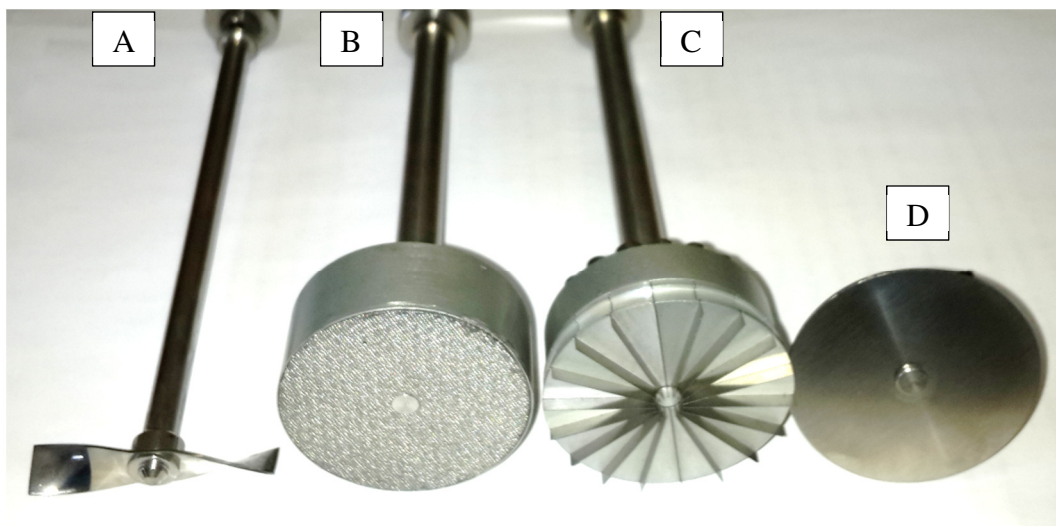


Figure 3-4 The testing mechanisms (48mm) used by the FT4 powder rheometer. A: rheometer blade. B: vented piston. C: shear cell. D: Wall friction disc.



Figure 3-5 Split vessel assemblies used by the FT4 powder rheometer. Left: 85mL split vessel in the open position. Right: 160mL split vessel in the closed position.

3.6.1 Repeatability and variable flow rate (dynamic analysis)

In this test, a 160ml split vessel (Figure 3-5) was used to ensure reproducible powder bed height and volume. A mass of powder was introduced into the vessel, the excess split off, and the retained sample weighed. Using the dynamic analysis test method, the powder bulk was subjected to a conditioning cycle, where the blade displaced the powder to establish a reproducible and uniform state, removing any previous packing history or inhomogeneity within the bulk powder [70, 73]. The blade then downward traversed the powder bed, at 100mm/s tip speed and a 5° helix angle, imposing deformation and flow upon the powder bulk as the blade passed through it, along its pre-determined helical path, as shown in Figure 3-6.

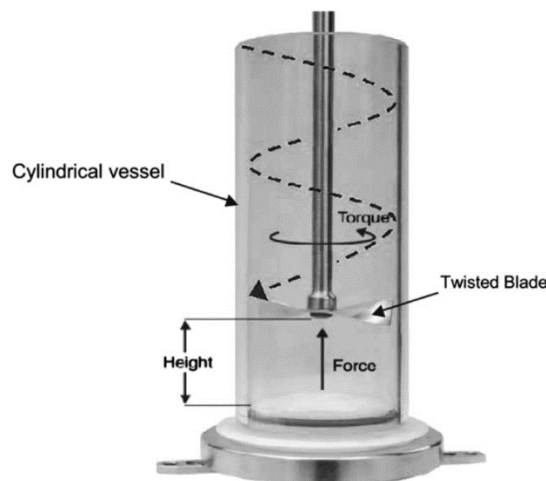


Figure 3-6 Schematic of the FT4 powder rheometer blade in downward motion [70].

The forces used to move the blade were then used, by the rheometer, to calculate the flow energy of each powder that was tested. The test cycle (downward motion of the blade at each tip speed) imposed compressive forces onto the powder bed (due to the blade shape and design), forcing the powder to move around the blade in order to flow. The recovering upward motion then lifted and de-compressed the powder. The test, using a tip speed of 100mm/s, was repeated several times to assess any fluctuations in the powder bulk while testing at a constant speed,

following which the speed was reduced to 70, 50 and then finally 10mm/s for subsequent tests. The change in tip speed yielded an indication of the powder flow energy change at decreasing flow rates. Such results can be used to calculate the powder's stability index, basic flowability energy and flow rate index [69, 70, 73-75]. Basic flowability energy (BFE, mJ) is defined as the energy needed to displace a conditioned powder sample during downwards testing (compression) using the bulldozing action of the rheometer blade [75]. Specific energy (SE, mJ) is the energy associated with the lifting action of the rheometer blade during upwards testing therefore this energy is a measure of powder cohesion [70]. Stability index (SI) is defined as the factor by which the flow energy changes when the powder is repeatedly tested, while flow rate index (FRI) is the factor by which the powder flow energy changes when the rheometer tip speed (flow rate) is reduced by a factor of ten [75]. Leturia et al. [70] noted that normalized basic flowability energy (NBFE, mJ/g) accounts for the differences in powder masses between samples, by taking the quotient of BFE and the powder sample mass, yielding a measure of the energy needed to move each gram of powder.

3.6.2 Shear stress

Shear tests were carried out using the 48mm shear cell accessory of the FT4 powder rheometer, as shown in Figure 3-7.

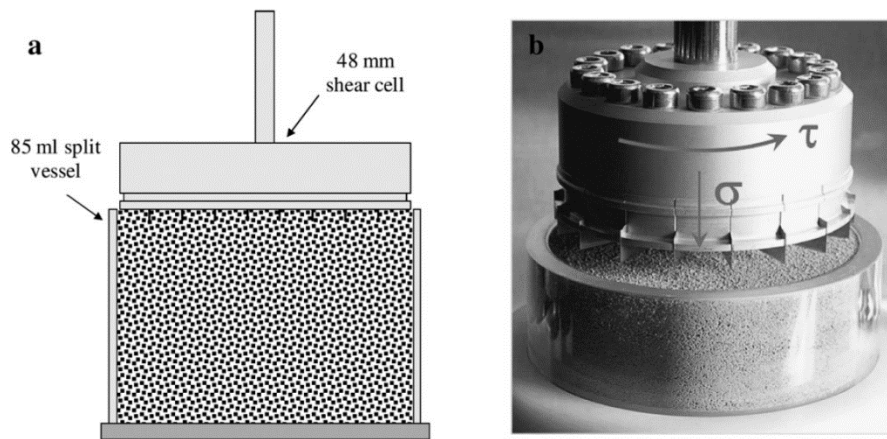


Figure 3-7 A: Schematic diagram and B: The rotational shear cell setup of the FT4 powder rheometer [70].

Further details of the shear testing apparatus and theory can be found elsewhere [69, 70, 73]. In this test, the powder was initially conditioned, then compacted slightly using a 15kPa force and a vented piston. The vented piston was produced from a woven stainless steel mesh that allows for air to escape the powder bed uniformly under pressure, while simultaneously compacting the powder bed slightly to a consolidated state suitable for shear testing [54]. The residual powder was then split off by opening the split test vessel to reveal a smooth powder test surface, and the shear cell was installed. Shear tests were performed from 5 to 15kPa with a shear rate of 18° per minute for 30°. Using Mohr's circle analysis with the generated yield loci of powders, various powder parameters other than the basic shear curve, can be extracted from the shear test such as major principal stress, unconfined yield strength, cohesion strength and angles of internal friction [70].

3.6.3 Compressibility

Compressibility tests were performed using the 48mm vented piston assembly, as shown in Figure 3-8.

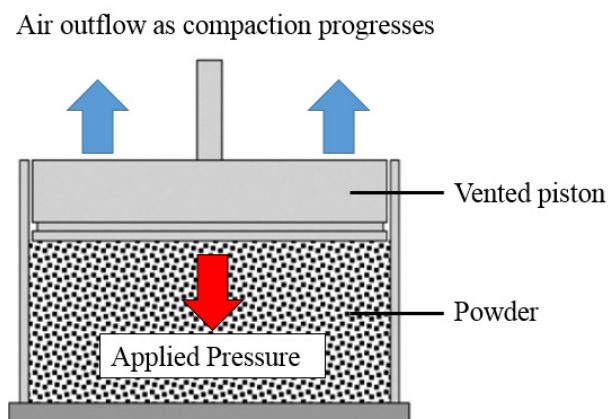


Figure 3-8 *Vented piston schematic: as pressure is applied, the powder bed releases entrapped air, which escapes through the vented piston.*

Powders were initially conditioned, the residual powder split off using the split vessel assembly, and then tested at pressures of 0.5 to 15kPa. The % powder compaction as a function of applied pressure was measured by the rheometer at each pressure increment.

3.6.4 Aeration and de-aeration testing

All aeration related work was performed with the standard 50mm aeration base to which the aeration control unit was attached via an air input hose. The aeration base replaces the standard plastic sample holder bases with a porous stainless steel mesh, allowing air to be pumped through it and into the powder bed from the bottom of the test vessel. The aeration control unit regulates the flow rate of air to the sample vessel.

3.6.5 Aeration / fluidization

Three versions of the aeration test were performed because of the differences in particle size, and consequently particle weight, of the various test samples. This was necessary since initial testing showed that after powder fluidization, if the air

flow was then increased, the powder sample was violently ejected from the sample vessel, which was more prevalent for the smaller, lighter particles such as the 45-63 μ m screen fraction of the powders. An air flow speed of 40mm/s was used for the largest particle size fraction (150-180 μ m), 30mm/s for the 90-125 μ m particles, and 15mm/s for the 45-63 μ m size fractions. The maximum air flow rate design limit for the aeration control unit was 40mm/s.

3.6.6 De-aeration (air retention)

The de-aeration test was essentially the same as the dynamic test method using the blade to traverse the powder bed at 100mm/s. Forces and flow energy were measured as before, except that the powder was subjected to air flow at 5mm/s for a conditioning cycle before the first test. The air flow then was turned off and the powder test performed (a downward and then upward blade traverse). The first test measured the powder in the aerated state. A second run was then performed in which the powder was again aerated during a conditioning cycle. Then the air flow was turned off, and the powder subjected to a single conditioning cycle to remove some of the air, after which the actual measurement cycle was performed. The third test used two conditioning cycles after aeration (in which the air flow was off) - hence allowing for an extra conditioning cycle compared to the previous test, to remove the entrapped air in the powder. The next test allowed for 3 conditioning 'de-aeration' cycles before testing, and so on. Hence, each extra conditioning cycle before each test allowed for more retained air to be released each time. The flow energy change with each test therefore indicated the ease with which the powder surrendered its entrained air. Powders were tested up to and including 5 de-aeration cycles.

3.6.7 Permeability

Permeability testing made use of the 48mm vented piston, applied to the prepared powder bed at a range of pressures from 1 to 15kPa, with an air flow rate of 2mm/s. The vented piston was held at each applied stress level for 60s to allow the powder bed to reach equilibrium, after which the applied normal stress was increased incrementally. The pressure drop across the powder bed was calculated by the rheometer, as the input air speed was kept constant. The ease with which air could permeate through the powders was then reported by plotting the measured pressure drop across the powder bed against the applied normal stress.

3.6.8 Wall friction

The 15kPa wall friction test routine of the FT4 powder rheometer was used for this test, with a wall friction head of 0.28 μ m surface roughness. The powder was conditioned and then pre-consolidated using the vented piston, and the residual powder was split off using a split powder vessel, leaving an exact mass of powder for testing. The test routine then compressed the powder to a maximum normal stress, greater than the largest applied normal stress needed for the experiment. This was done in order to compact the powder sufficiently to achieve a steady state and reproducible results [83], following which the measurements were performed as a function of decreasing applied normal stress, starting from 15kPa and then decreasing from 9kPa in 1kPa increments down to 5kPa. During the measurements the pressure was held constant for 25s without rotation to allow for the powder to reach equilibrium. The wall friction head was then rotated and the torque increased as the powder / head interface resisted motion. Under these conditions, after maximum torque was attained, failure (slippage) occurred. The wall friction head was then rotated for 5° at a rate of 18°/min at the ‘steady state’ shear stress i.e. the shear stress closest to the failure stress, but where steady rotation at the required pressure can still occur and be measured reproducibly [83]. The torque required to turn the wall friction head was measured by the rheometer,

following which the shear stress imposed on the powder was returned to zero by reversing the head direction and then repeating the test procedure at the next (lower) applied normal stress. The wall friction angle (Φ) was calculated by the FT4 rheometer software using the shear stress (torque, τ_w) plotted against the applied normal stress (σ_w) for the series of applied normal stresses tested, according to the equation:

$$\Phi = \tan^{-1}(\tau_w/\sigma_w) \quad (4)$$

3.7 Pressing

Two compaction techniques were used during this study, the first was the standard production conditions used to manufacture cemented carbide mining buttons in order to prepare the bulk materials for recycling, and the second was a pressing test across a wide shrinkage range for further powder characterization.

3.7.1 Bulk pressing

A 7 x 9.7mm mining button, multi-cavity tool was used to uniaxially press the NP-lab powder in preparation for zinc recycling. The powder was pressed at 20% shrinkage, using a Fette MP-250 hydraulic press equipped with a Roboworker R.A.G.2 ‘pick and place’ robotic arm.

3.7.2 Pressing tests

Using the same press and robot apparatus as above, a single cavity cylindrical test was used to produce test pieces of 10mm diameter. The pieces were uniaxially pressed at different shrinkages (17-26%) in order to determine the pressing force required for optimum consolidation of each powder.

3.8 Sintering

All samples in this work were sintered in Ultratemp (USA) sinter-HIP furnaces. The furnaces were initially heated to 1200°C at a rate of 2.4°C per minute after which cobalt loss protection by the addition of argon gas at 0.37MPa pressure was engaged, with a heating rate of 3.5°C per minute up to a final sintering temperature of 1430°C. The sintering temperature was maintained for 75 minutes, and then during the last 20 minutes, the argon gas pressure was increased to 4.4MPa for hot isostatic pressing. The furnace was then cooled to room temperature at a rate of 3.5° per minute.

3.9 Sintered sample analysis

3.9.1 Density

Sintered sample densities were determined using the Archimedes principle on a Shimadzu AY120 4 decimal place scale equipped with an automatic density suspension and reporting system. Three samples of each grade were analysed, and the average result and associated error have been reported.

3.9.2 Magnetic saturation and coercivity

Magnetic saturation of the sintered cemented carbide samples was measured using a Setaram 6461 cobalt magnetic saturation machine, equipped with a Sigmameter digital controller and a Scout Pro SPU402 digital balance. Magnetic coercivity of the sintered samples was measured using a Dr. Förster-Koerzimat coercimeter.

3.9.3 Sintered sample polishing

Sintered samples (cylinders) were cut in half (axially), mounted in Bakelite resin, ground, and then polished using decreasing grit size progressively to a final surface finish of 1µm.

3.9.4 Vickers hardness

Vickers hardness was measured using a Mitutoyo AVK-CO hardness tester with an applied load of 30kg force, held for 30 seconds. The Vickers hardness was calculated using equation 5, with the average hardness of three indentations per sample reported.

$$H_V = \frac{1854.4F}{d^2} \quad (5)$$

Where: F = applied load (kg)

d = average diameter of the diagonals (mm).

3.10 Analytical techniques

3.10.1 Micro-PIXE

Micro-PIXE was performed using a nuclear microprobe (NMP) at the Materials Research Department, iThemba LABS, Somerset West, South Africa. A proton beam of 3.0MeV and current of 100 - 200pA was focused to a 3x3µm spot and raster scanned over selected areas of interest. The number of pixels varied up to 128x128. Micro-PIXE and proton backscattering were used simultaneously. Normalization of results were done by using the integrated beam charge (digital

signal), collected from the insulated specimen holder. Experimental acquisition data were collected in list-mode (event-by-event) using the XSYS data acquisition system and then processed using the GeoPIXE II [84]. Elemental maps demonstrating patterns of elemental distributions were generated off-line using the Dynamic Analysis method [85]. Mean true elemental concentrations in WC-Co spheres were evaluated by selecting particular regions within the matrix of the spheres wall and full deconvolution of the micro-PIXE spectra. Other experimental details related to the nuclear microprobe experimental set up have been described earlier [86].

Elemental composition was extracted from a circular area of the granule wall. Micro-PIXE was used to detect 3 main types of elements: (i) major constituents of intentionally added materials (e.g. W, Co), (ii) additional alloying elements such as Ti, Nb, and Ta were detected at the wt% level, and (iii) trace impurities of the processed materials (ppm level). Elemental maps were generated of 300x300 μm areas and were reconstructed off-line with the software package Geo-PIXE II V 6.4.

Micro-PIXE was used to map the sintered microstructures of the various alloys, as well as oversize material, and acetic acid leached cylinders, using scan areas of 25 x 25 μm to 1000 x 1000 μm .

3.10.2 SEM analysis

Two scanning electron microscopes were used during the course of this work. A Carl Zeiss field emission scanning electron microscope equipped with an Oxford X-act energy dispersive spectrometer (EDS) and a Nova NanoSEM 230 equipped with an Oxford X-Max silicon drift EDS detector. Accelerating voltages of 20keV were used whilst EDS was used for composition analysis. Micrographs of the internal granule structure and the sintered microstructures was characterized using backscatter mode.

3.10.3 X-ray diffraction

X-ray diffraction used for phase identification was performed using a BRUKER D8-ADVANCE diffractometer coupled with a Vantec-1 position sensitive detector. Data was collected between 15° and 100° in 2θ with a 0.02° step size using $\text{CuK}\alpha$ radiation at 40kV and 40mA. XRD was performed on the milled powders as well as each sintered compact.

3.10.4 ICP-OES

The chemical composition of the powders was analysed using a Thermo Electron ICAP 6300 radial inductively coupled plasma spectrometer utilizing iTeva (Thermo electron) software. Carbon and sulphur content was determined using an Eltra Metalyte CS 1000 carbon-sulphur analyser.

4. RESULTS

4.1 Introduction

The results of an initial study into the use of the micro-PIXE technique for cemented carbide characterization are presented first, followed by the results of the zinc recycling and acetic acid recycling processes. Powder characterization results are then presented, with slurry and powder rheology chapters following in their own dedicated sections. Finally, sintered materials characterization results are presented.

4.2 Initial study assessing the micro-PIXE technique

Initial studies using micro-PIXE were performed, to evaluate the performance and sensitivity of the technique on WC-Co powders. To the author's knowledge, the use of the technique in this way is novel, requiring some evaluation of the technique before it was to be used to compare the project's primary materials. Spray dried tool grade (TG, referring to a material containing cubic carbides) and straight grade (SG, referring to a WC-Co composition only) powders were studied, with emphasis on detection on the major constituents as well as impurity levels. The TG powder was produced from fresh, new powders. The SG powder was zinc recycled mining scrap, blended to a WC-6wt% Co composition, the same grade used throughout this project. A SEM micrograph and elemental maps for the recycled mining grade powder are shown in Figure 4-1; similarly the tool grade powder is shown in Figure 4-2, in which the W_L map is also shown to demonstrate the dominant element in micro-PIXE mapping. Table 3 (page 70) shows the overall elemental concentration comparison of the circular regions indicated for each powder.

Observing Ti concentrations in the recycled and tool grade powders, despite pre-recycling and sorting processes, Ti entered the SG material, with an average concentration of 0.13wt% (Table 3) compared to 5.12wt% in the TG powder. Titanium was well distributed within both powders. Iron contamination was evident, indicating the build-up of iron in recycled material (using the zinc method); similarly increased Ni concentration in the recycled grade was detected while none was detected in the tool grade powder (Table 3). Iron was detected in the tool grade powder, but with an average of only 338ppm compared to 0.21wt% in the SG powder. Trace elements Cr, Cl, Ca, and S were detected in the recycled powder but not in the tool grade powder.

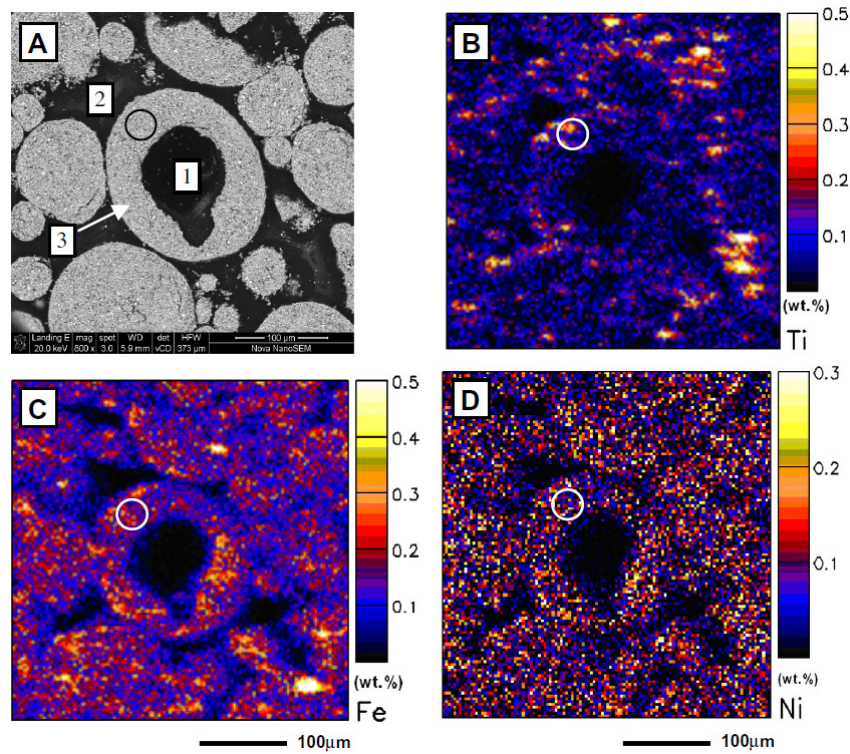


Figure 4-1 A: SEM micrograph of the recycled straight grade powder. A-D: Corresponding micro-PIXE elemental maps and location of the region (circle) used to extract the powder composition (Table 3). 1: the internal void of the granule, 2: copper/epoxy resin, 3: granule wall.

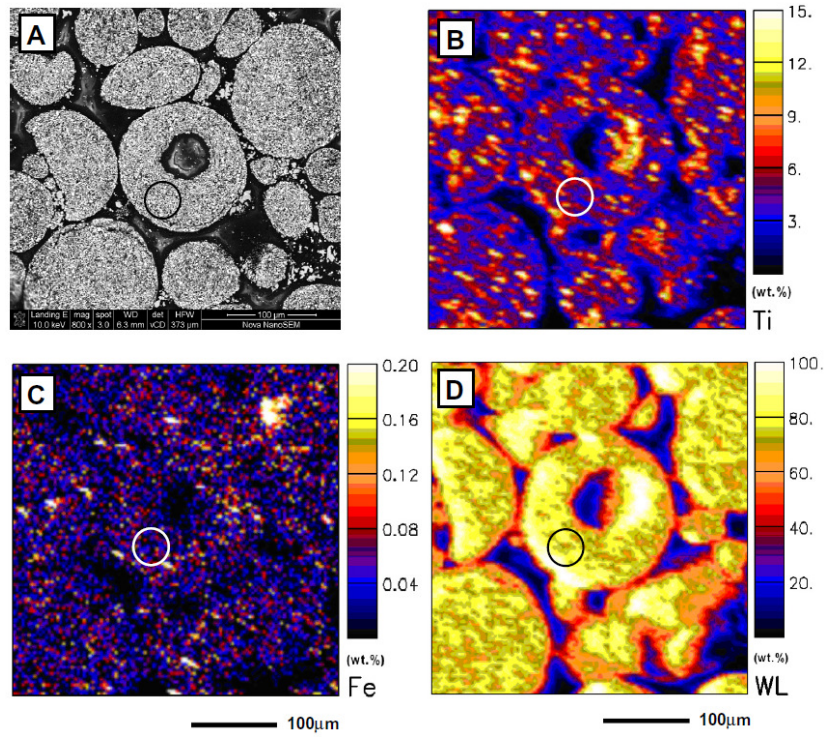


Figure 4-2 A: SEM micrograph of the tool grade powder. A-D: Corresponding micro-PIXE elemental maps and location of the region (circle) used to extract the powder composition (Table 3).

Table 3: Extracted elemental composition of the circular regions (Figure 4-1 and 4-2) with errors and minimum detection limits (in brackets) for the recycled straight grade and tool grade powders.

Element:	W	Co	Ti	Ta	Nb	Cu
SG	89.77 ± 1.08 (0.05)	6.66 ± 0.01 (0.01)	0.13 ± 0.01 (0.01)	ND	ND	0.12 ± 0.01 (0.02)
TG	78.44 ± 0.09 (0.03)	7.59 ± 0.02 (0.004)	5.12 ± 0.02 (0.006)	2.65 ± 0.03 (0.04)	0.31 ± 0.05 (0.10)	1521 ± 0.01 (0.01)
Element:	Fe	Ni	Cr	Cl	Ca	S
SG	0.21 ± 0.01 (0.01)	0.09 ± 0.02 (0.02)	0.02 ± 0.01 (0.01)	0.05 ± 0.05 (0.05)	0.04 ± 0.01 (0.02)	1.23 ± 0.11 (0.09)
TG	338 ± 0.002 (0.004)	ND	ND	ND	ND	ND

The preliminary investigation (explored in detail in the discussion chapter) showed that micro-PIXE could accurately detect both trace and major elements to a ppm degree of accuracy.

4.3 Zinc recycling process

The zinc recycling process typically achieves a yield of greater than 95% on small to medium sized components (up to 15mm thick) at Pilot Tools (Pty) Ltd and was successfully performed to produce all the zinc recycled feedstock powder materials for this study. The availability and nature of scrap material, however, determines the efficiency of this process, and large scrap parts can result in by-product materials. This section provides analysis of the oversize (PRZ-by-product) materials, which were used as feedstock for the acetic acid recycling process. The detailed analysis of the PRZ materials is presented in later sections, in comparison with the other materials.

Two types of oversize material form in the zinc recycling process at Pilot Tools (Pty) Ltd. Dense oversize forms when zinc does not penetrate the sample to its center, leaving a hard and dense core. Porous oversize results when zinc penetration reaches the sample center, but the sample still does not break down mechanically. Both types of oversize materials have been investigated.

Optical micrographs of the dense and porous oversize samples are shown in Figure 4-3. The core region is clearly visible for the dense oversize sample (Figure 4-3 A), with successive microstructural layers progressing outward toward the porous extremities. The porous oversize sample (Figure 4-3 B) can be seen to still contain some denser regions, but is predominantly porous throughout its structure.

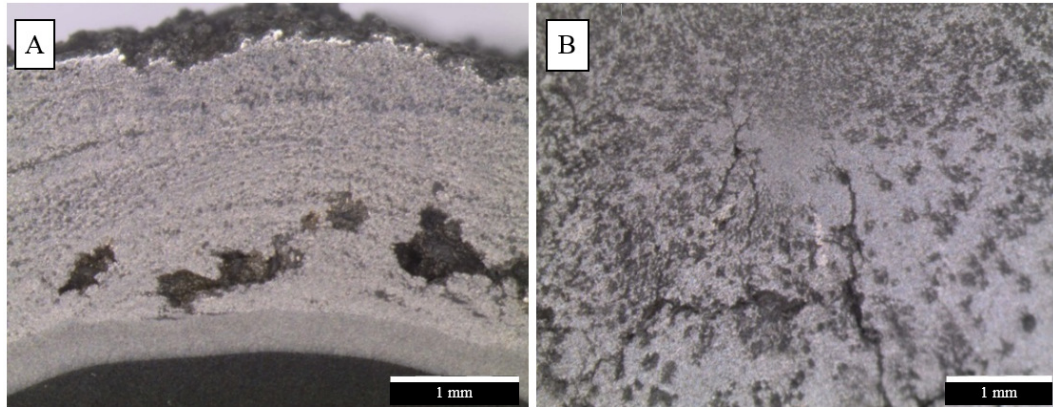


Figure 4-3 Optical micrographs of A: dense oversize material showing a layered structure and B: porous oversize material.

A SEM micrograph of the core region of the dense oversize sample is shown in Figure 4-4, with the corresponding elemental micro-PIXE maps for W_L and Co. The level of cobalt present indicates that the original sample (before zinc recycling) contained approximately 10 to 15wt% Co, which is typical for WC-based mining tools, which usually range from 6 to 15wt% Co, depending on the application. The zinc content at the core was measured as negligible and the original cemented carbide microstructure was intact, indicating that zinc did not penetrate to the core. Some porosity was noted within the core.

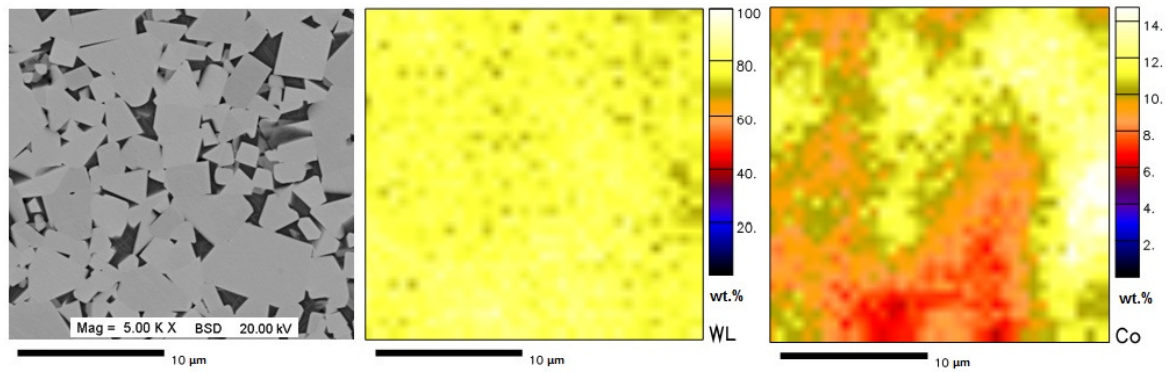


Figure 4-4 SEM micrograph and micro-PIXE elemental composition maps for W_L and Co, showing a typical WC-Co microstructure, measured in the core of the dense oversize sample.

Figure 4-5 shows a SEM micrograph and accompanying micro-PIXE maps, for the core region and the surrounding layered structure. Three layered regions have been categorized according to cobalt content. Region A, the dense core with around 10 to 15wt% Co, Region B (approximately 15 to 30wt% Co) showing fine lamellae with physical separations between the layers, and Region C, a cobalt rich region with 30 to 60wt% Co showing a layered, porous structure that initially shows finely divided WC and Co layers, becoming coarser towards the sample surface. An inverse relationship between the W and Co compositions can be seen in the micro-PIXE maps, Figure 4-5, in which the cobalt content increases with each layer moving outward from the core.

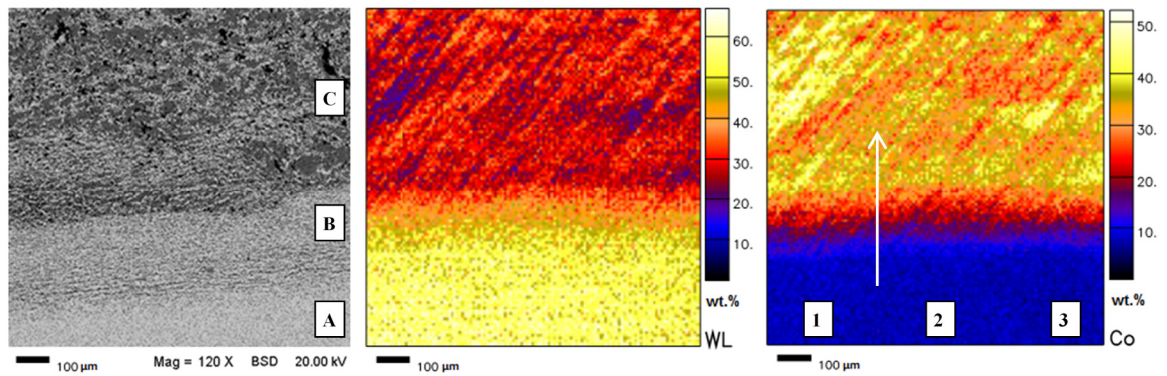


Figure 4-5 SEM micrograph of the dense oversize sample with defined layered regions namely: A: the core, B: a region of finely divided WC-Co layers with visible cracking and separation, and C: a porous, coarsely layered WC-Co structure close to the sample surface. Corresponding micro-PIXE maps are also shown for W_L and Co.

Figure 4-6 shows a micro-PIXE map of the outer layered region C. The SEM micrograph in Figure 4-6 (high magnification image of the squares indicated on the adjacent micro-PIXE maps) shows the microstructural features giving rise to the layered effect, i.e. repeating layers of WC grains (angular shapes, light grey) and Co binder (globular, dark regions).

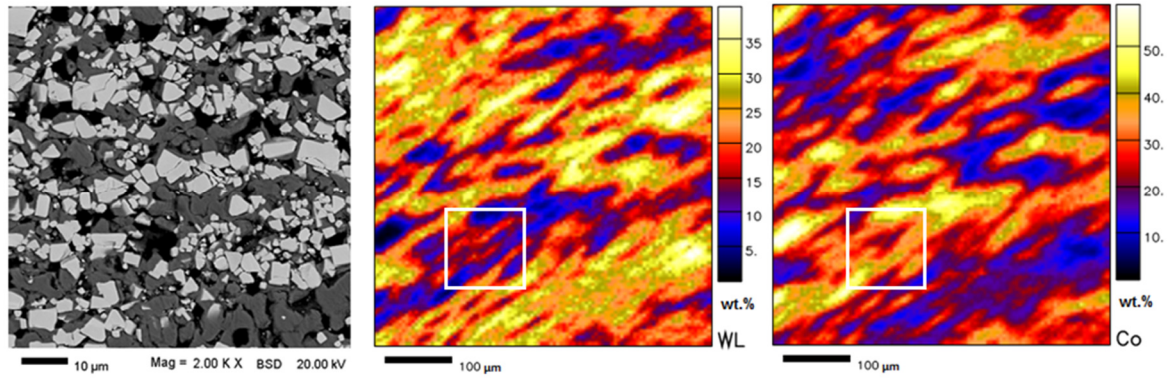


Figure 4-6 The outer region of the dense oversize sample (Region C on Figure 4-5) showing a high magnification SEM micrograph (square region on the micro-PIXE maps) illustrating alternating layers of WC grains and Co binder, and the micro-PIXE maps of region C.

Micro-PIXE indicated that Co concentrations approaching 60wt% occur in the cobalt-rich layers and W concentrations around 40wt% in the tungsten-rich layers. Therefore, micro-PIXE detected a far higher cobalt content in region C than the composition found in the core (10 to 15wt% Co). Micro-PIXE line scans were performed as shown on Figure 4-5. The scan was performed 3 times at positions 1 - 3 as indicated on Figure 4-5, across 1mm of sample with the arrow indicating the scan direction. The average results and errors are presented in Figure 4-7. The origin of the graph (Figure 4-7) corresponds to the start of the line scan, i.e. from within the core of the sample at the bottom of Figure 4-5.

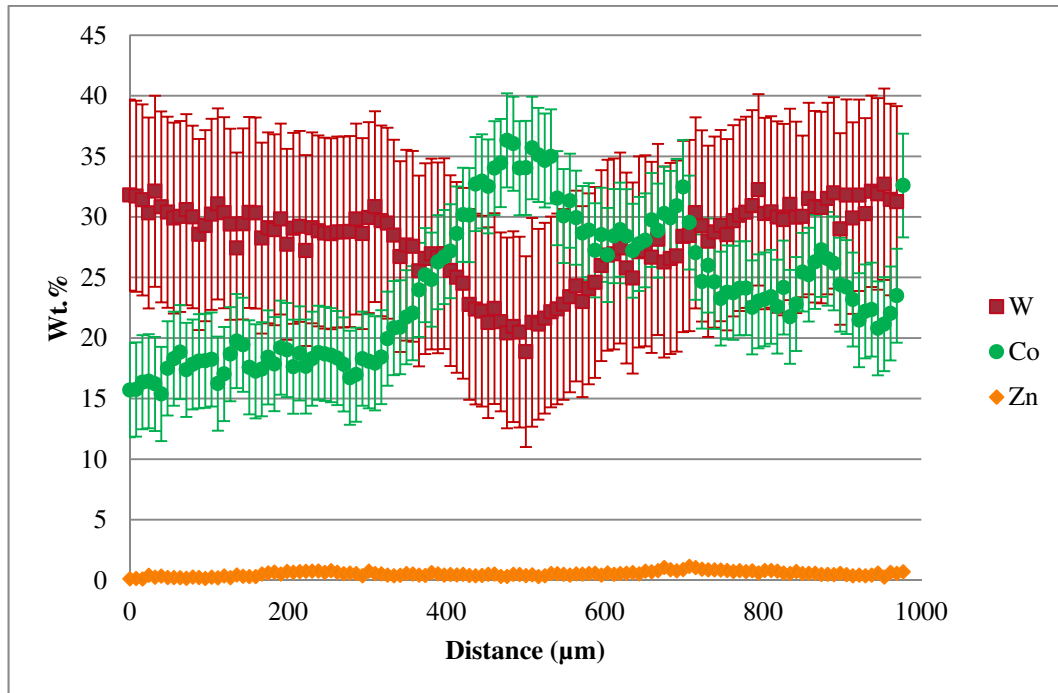


Figure 4-7 Average micro-PIXE line scan of zones 1-3 in Figure 4-5. Iron and Zn were the main impurities detected. The iron and zinc traces overlapped, hence only zinc had been shown for clarity.

Zinc and iron concentrations fluctuated across the scanned region between 0 to 1wt% and 0.5wt% respectively. Cobalt increased steadily within the core, up to a value of approximately 20wt% Co. As the scan crossed the interface between the core and the layered structure, cobalt increased sharply to ~35wt%, in inverse relation to the W content.

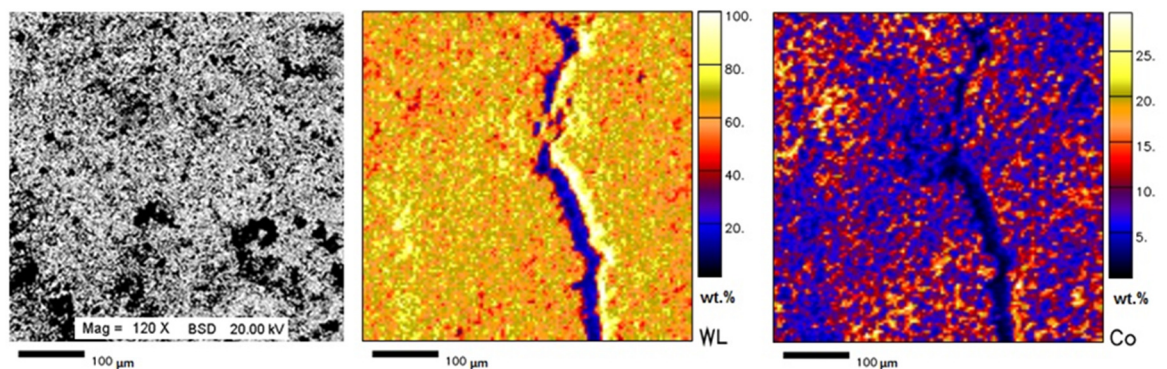


Figure 4-8 SEM micrograph and micro-PIXE maps of porous oversized material.

Figure 4-8 shows a SEM micrograph and micro-PIXE maps of the porous oversize material. The porous oversize had extensive cracking, with SEM and micro-PIXE showing no clear cobalt gradients. Cobalt-rich clusters can be seen in the micro-PIXE maps, with some clustering occurring around the crack. Zinc levels less than 0.1wt% were detected in this sample, indicating that zinc was more successfully withdrawn from the porous oversize material than the dense oversize material.

4.4 Acetic acid leaching

This section presents the results of the acetic acid leaching experiment, in which pH monitoring and leaching rates of sintered cemented carbide buttons were measured and analysed. The material comparison between the acetic acid material and the other materials is presented in later sections.

4.4.1 pH monitoring

The pH and temperature of the acetic acid plant were checked regularly during the 21 days of leaching. Figure 4-9 shows pH curve across the 21 day period. Initially, the pH increased rapidly from a value of 1.85 to above 3.0 within 48 hours of leaching. The rate of leaching decreased between 50 and 150 hours, after which fresh acid was added to decrease the pH again to below 2.5. Despite the highly acidic conditions, the rate of leaching after 150 hours did not match the initial rate of leaching at any later stage in the run. The leaching rate was steady thereafter, with a notable increase in pH corresponding to a water top-up, necessary to prevent the acid plant liquid level from decreasing excessively, thus exposing the element - which could cause overheating and melting.

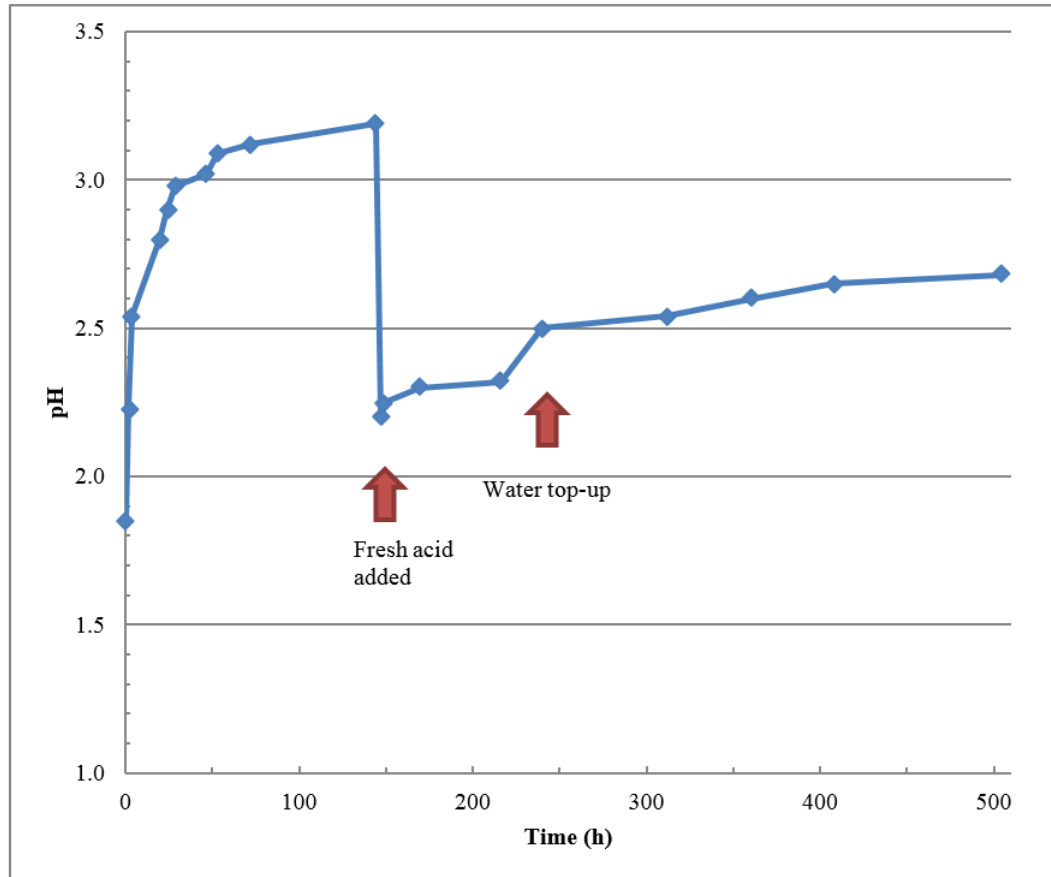


Figure 4-9 Graph of the pH variation for 21 days (504h) of the acetic acid leaching process at 80°C.

4.4.2 Leaching rate of sintered test samples

In order to monitor the progress of the acetic acid leaching process on fully dense WC-Co material, samples of WC-6wt% Co (NP-lab) material were suspended within the acetic acid bath in a sample basket, and extracted and examined at specific time intervals. Figure 4-10 shows the SEM micrographs of samples extracted on day 1, 7, 13, 17 and 21.

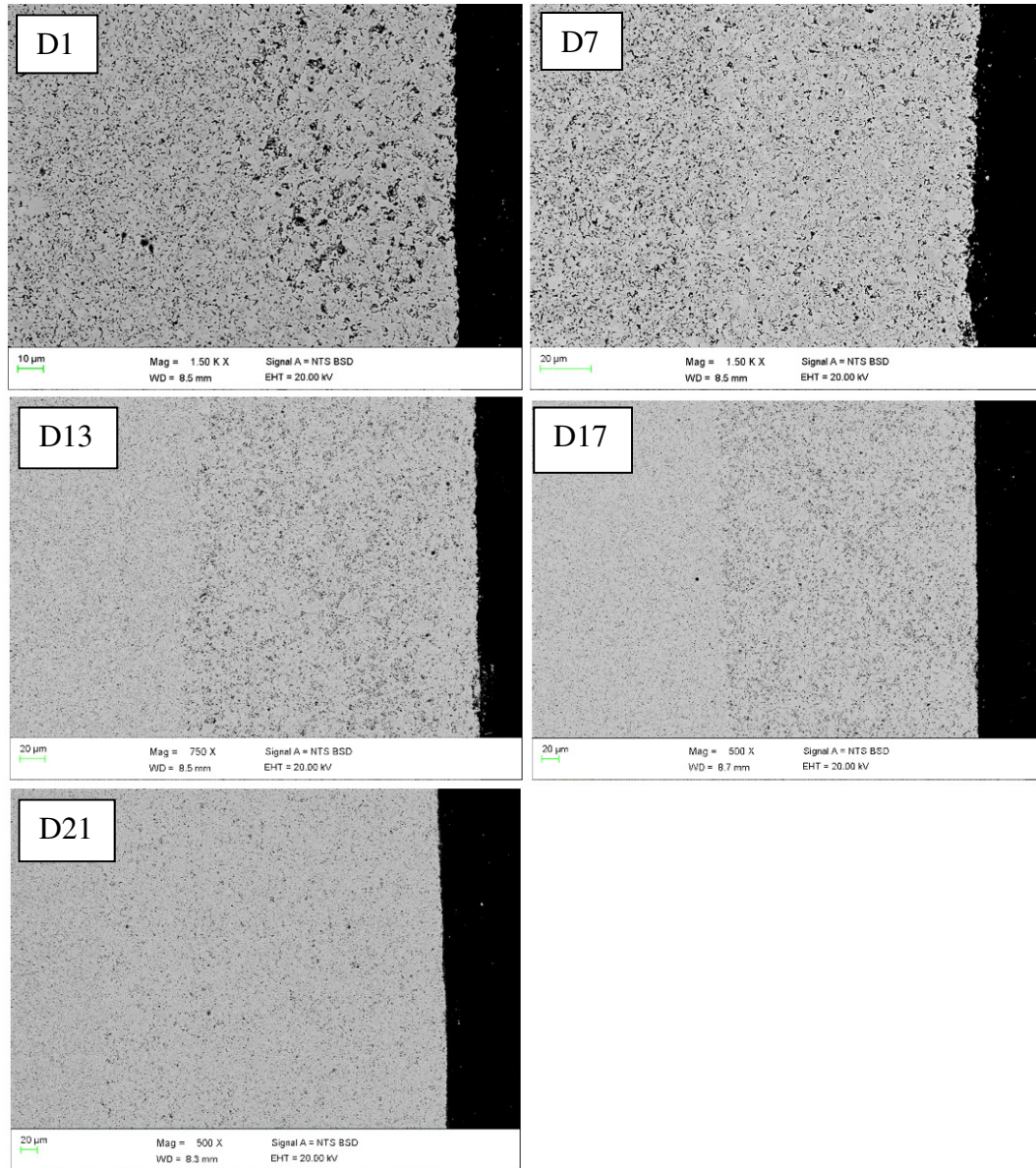


Figure 4-10 Progress of the leached layer of the sintered samples at various daily intervals during the acetic acid recycling run. The day is indicated by the letter ‘D’, for example D1 represents ‘Day 1’ etc.

The leached layer progressed inwards from the surface of the samples, as shown in Figure 4-10 by the porosity (dark spotted layer) where the cobalt binder was removed progressively with time. Figure 4-11 shows the micro-PIXE maps of day 13 (D13 from Figure 4-10) in which the abrupt termination of the leached layer met the unaltered cemented carbide core. The leached layer thickness did not

exceed 700 μm even after 21 days. The leaching rate achieved in day 1 of approximately 70 μm , was unmatched in the subsequent days, when the rate of leaching slowed down. Iron and some Nickel were also leached out with the cobalt as shown in Figure 4-11.

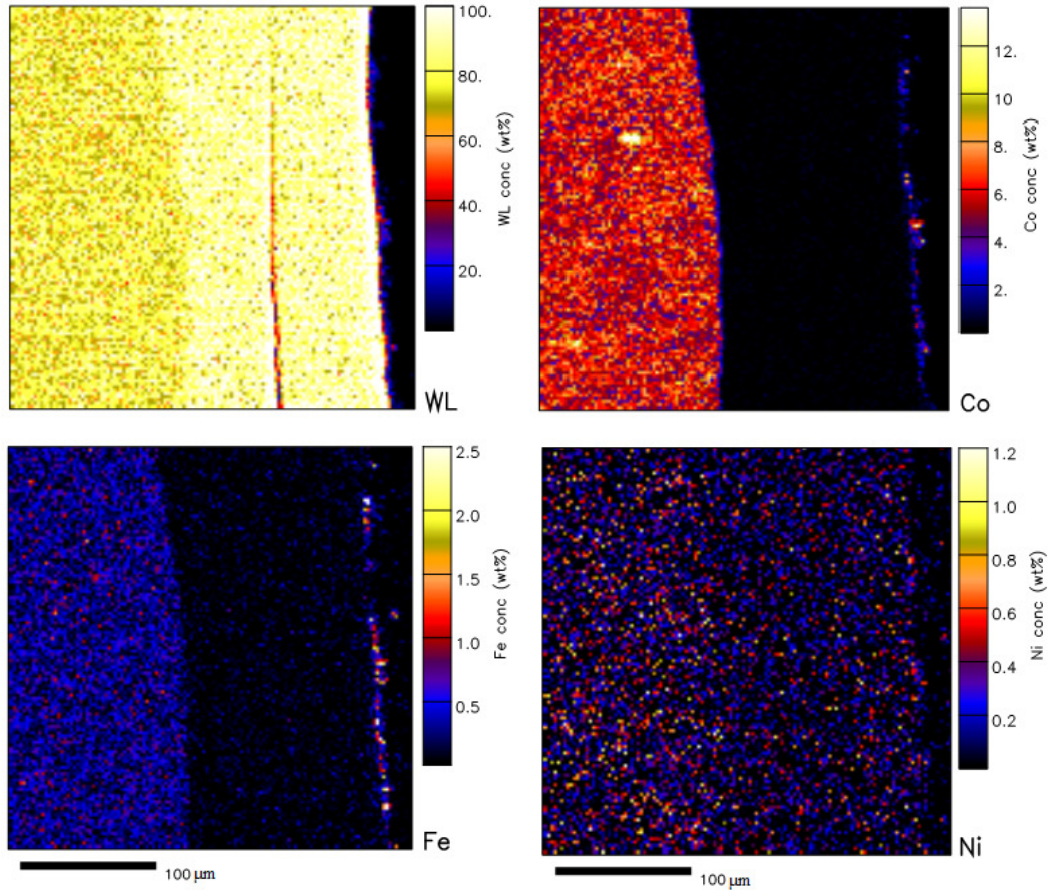


Figure 4-11 Micro-PIXE maps of the sintered WC-6wt% Co sample at day 13 of leaching.

The micro-PIXE maps corresponding to day 21 of the leached sintered material are shown in Figure 4-12, in which the interface of the unaltered core and leached layer were investigated. As with the day 13 sample, the cobalt was completely extracted up until the leached interface, and remained unaltered at the 6wt% level in the core. The acetic acid penetrated a thin layer (less than 10 μm thick) of WC-Co at any given time as indicated by the sudden interfacial layer between the

leached area and the core. No porosity was observed within the core adjacent to the interface.

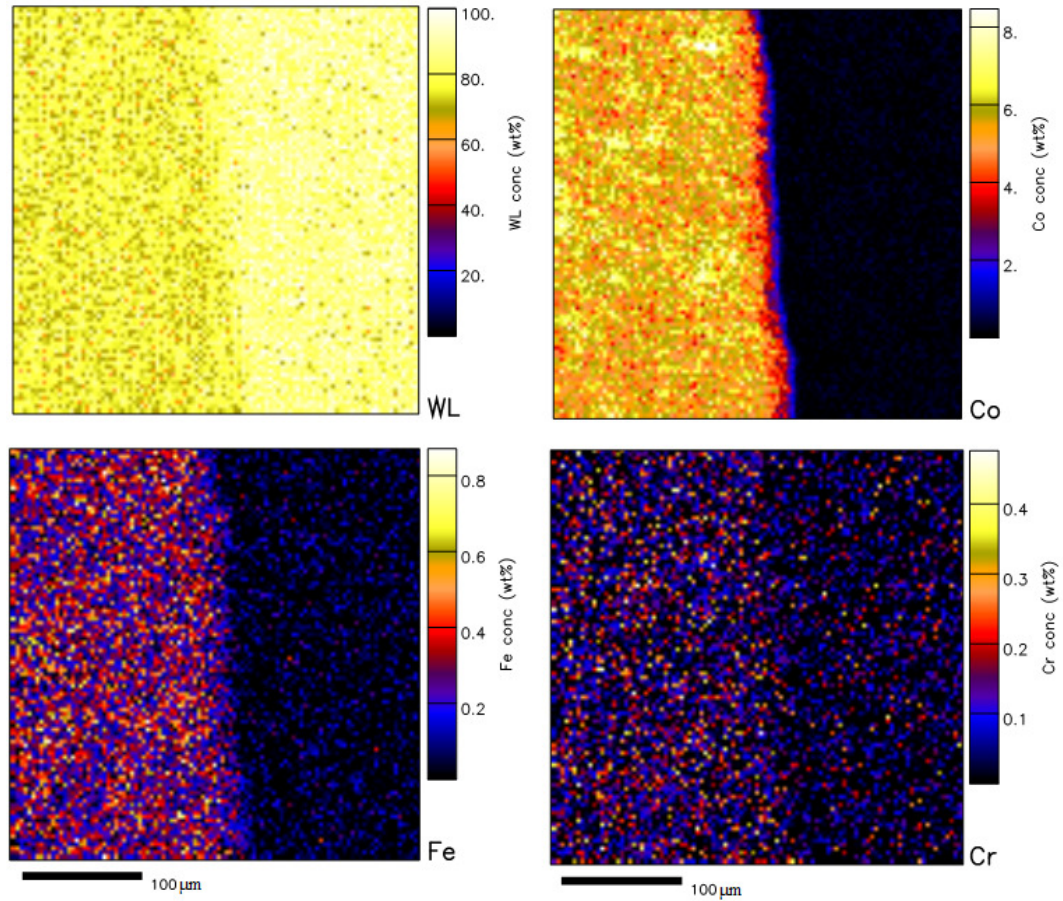


Figure 4-12 Micro-PIXE maps of the sintered WC-6wt% Co sample across the leached interface, at day 21 of leaching.

4.4.3 Leaching rate of oversize material

Various oversize samples were extracted from the acetic acid bath over the 21 day period. Porous oversize samples (Figure 4-13) were leached of most of their cobalt within the first ten days, further evidenced by the rapid change in pH of the acetic acid solution within the first 100 hours of the experiment, indicating a rapid initial reaction rate that can be attributed to the large reactive surface area of the porous oversize material. Some residual cobalt can be seen in the porous oversize

material after 7 and 9 days (Figure 4-13) but the material was easily broken up. Figure 4-14 shows dense oversize material samples after 17 and 21 days, each possessing a leached layer $> 200\mu\text{m}$, but retaining a predominantly dense core. The dense oversize material resembles the new cemented carbide parts that were exposed to the acetic acid, showing approximately 6 - 10wt% Co within the core, as evidenced by the micro-PIXE maps in Figure 4-15, and a cobalt depleted surface zone. The iron and nickel impurities were leached out of the dense oversize material in the same way as the new material. The dense oversize material did not break down fully under mechanical milling, despite 21 days of acetic acid leaching over and above the prior zinc recycling process. The cobalt depleted leached zone did, however, break down during milling, along with the porous oversize material.

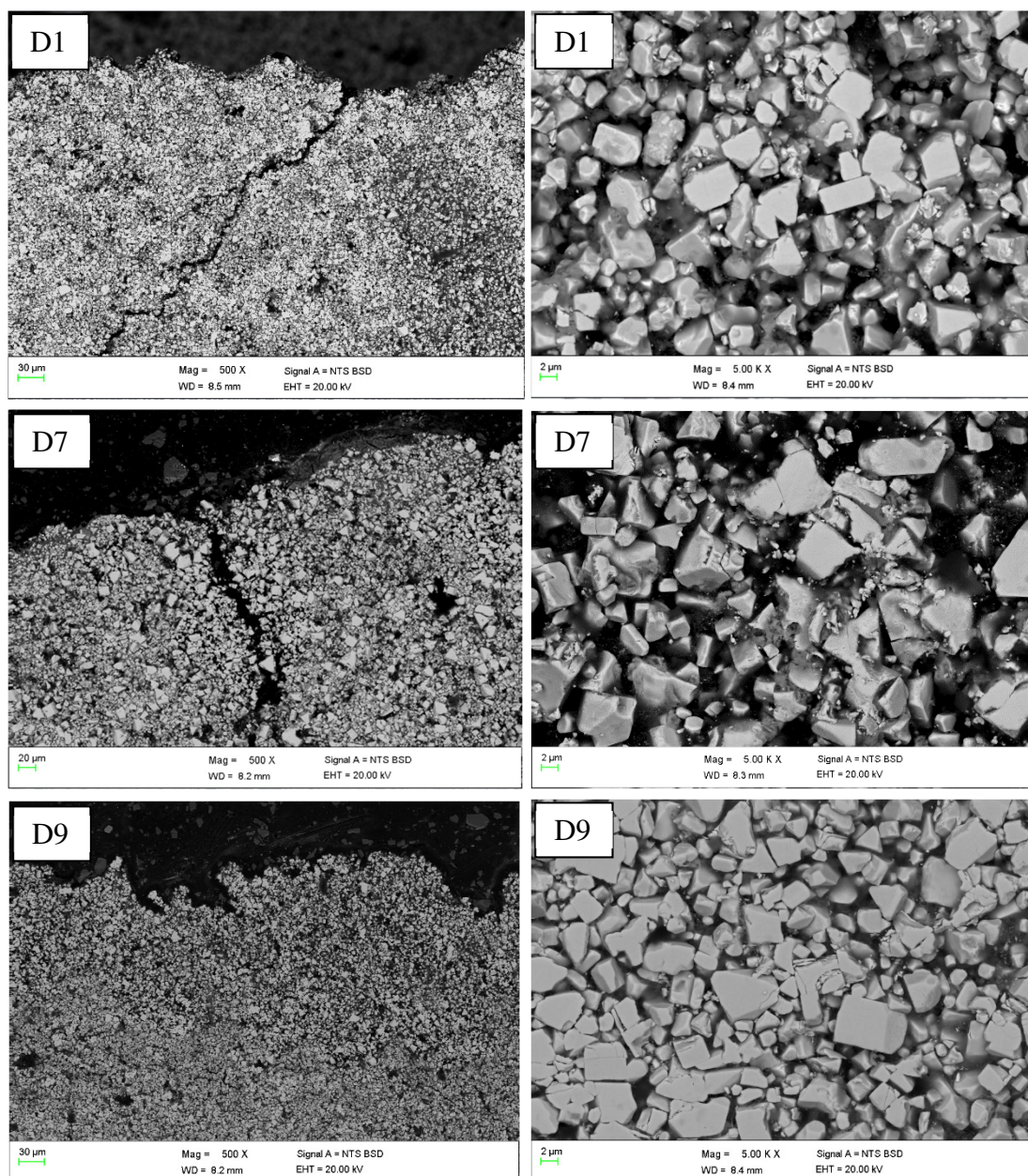


Figure 4-13 SEM micrographs of porous oversize samples acetic acid leached for 1, 7 and 9 days at 500X and 5000X magnification. Cobalt was rapidly leached out of the porous oversize materials within the first ten days.

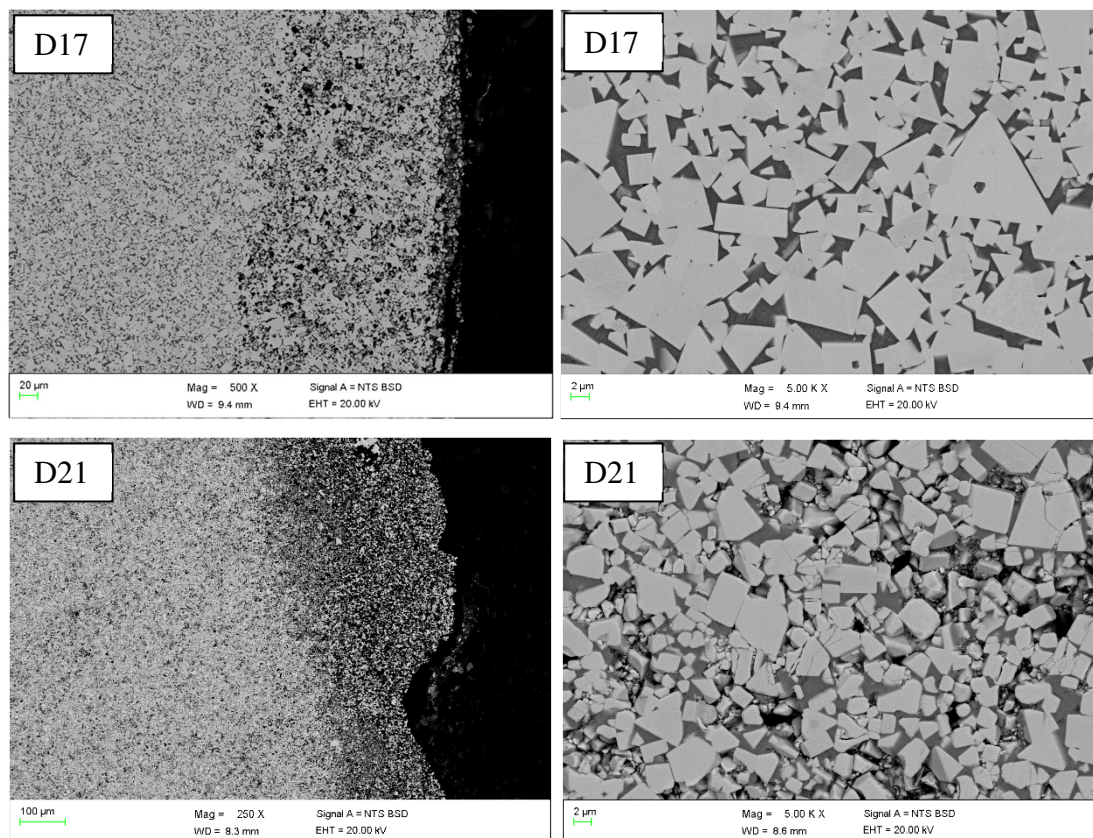


Figure 4-14 SEM micrographs of dense oversized material, partially leached but still retaining cobalt at 17 and 21 days of acetic acid leaching, at low magnification (250-500X) and high magnification (5000X).

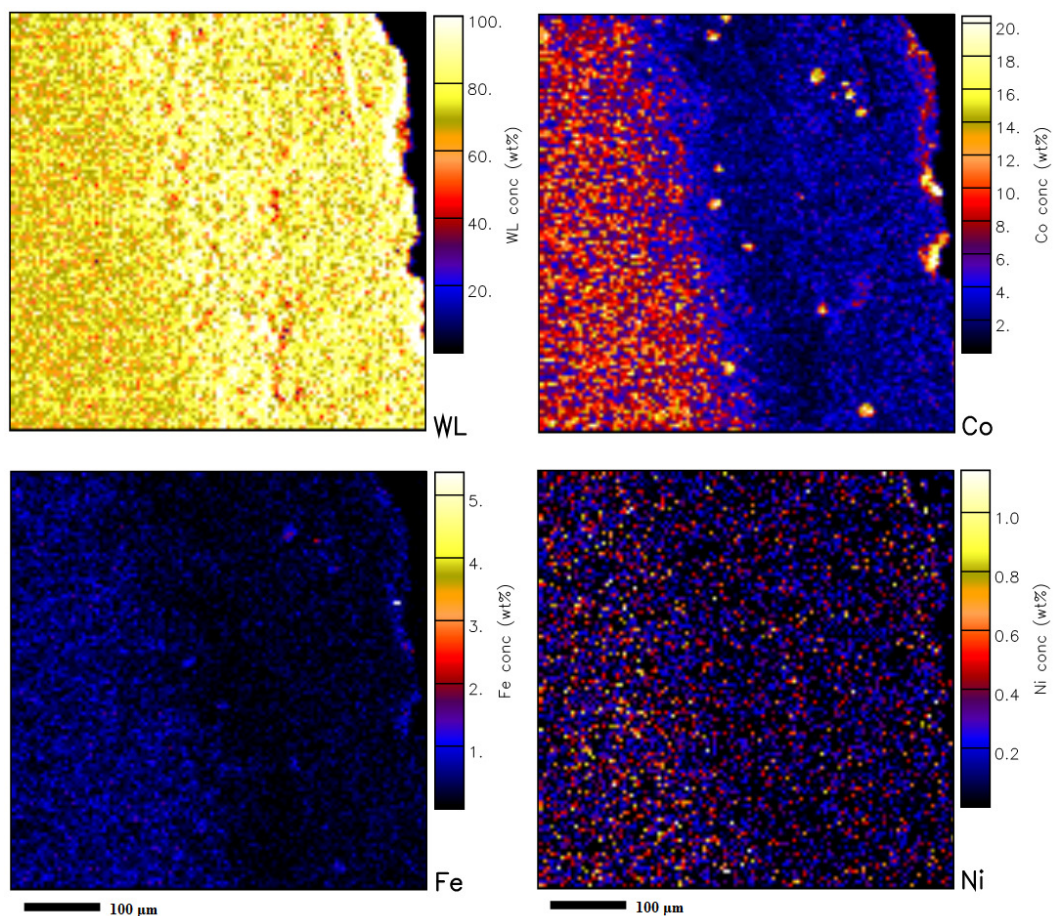


Figure 4-15 Micro-PIXE maps of a dense oversize sample after 21 days of acetic acid leaching showing the WL, Co, Fe and Ni distributions.

4.5 Powder material characterization

The results of the analysis of the feedstock powders as well as milled and spray dried powders are presented in this section. Chemical analysis is presented first, followed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and then micro-PIXE results. General bulk properties and microstructures of the spray dried powders are then presented, followed by the pressing test results.

4.5.1 Composition of powders

This section deals with the chemical and phase composition of the various powders.

4.5.1.1 New powders

Chemical analysis of the new 4 μ m WC powder and the Co raw material powders is shown in Table 4. The theoretical stoichiometric ratio of W to C in WC is 6.132wt% (or 50 atom %), hence, the WC powder was slightly above stoichiometric balance, with 0.03wt% free carbon present. The impurity elements were only present in trace amounts in the starting material.

Table 4: Elemental composition of the feedstock raw material powders.

WC starting powder

Element	W	TC	FC	S	Co	Fe	K	Mg	Mn	Cu
(ppm*)	93.82 wt%	6.14 wt%	0.03 wt%	10	5	42	5	5	5	5
Element	Ni	Mo	Na	Ca	Si	Cr	Al	O	N	
(ppm)	6	26	10	18	30	13	10	230	10	

Co starting powder

Element	Co	Fe	Cu	Zn	Ni	Mn	Pb	Ca	S	Mg
(wt%)	99.639	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.004	0.001
Element	Na	Si	Al	Cr	C	O				
(wt%)	0.004	0.001	0.002	0.001	0.020	0.320				

* unless otherwise stated as wt%; TC: Total carbon, FC: Free carbon

4.5.1.2 Milled and spray dried powders

The elemental composition of the milled and then spray dried laboratory and production milled powders with the removed polymers (PEG and dispersant were burned off prior to testing), are shown in Table 5 (which can be found on the following page).

Iron (Fe) and chromium (Cr) levels were highest in PRZ-lab followed by NP-lab and then AC-lab. The lowest levels recorded for these elements was for NP-prod. The nickel concentrations followed the same trend. The Fe and Cr levels in grade NP-lab were triple the amounts found in PRZ-prod and more than half the levels found in PRZ-lab. The recycled mining grade, PRZ-prod, contained the highest levels of Ta and Ti, AC-lab had the highest copper and vanadium contamination, while grade PRZ-lab had the highest levels of Ni. The sulphur and zinc levels were low for all of the grades. Carbon levels conformed to the chemical requirements for the grades, which, assuming no other impurities, should read at a theoretical value of 5.76 for a perfectly stoichiometric WC-6wt% Co grade. The W and Co levels were similar for all of the grades, with AC-lab being the only grade with slightly greater than the target 6wt% Co present.

Table 5: Elemental composition of spray dried powders (with removed polymeric binder).

Element	NP-lab	PRZ-lab	AC-lab
Ca (ppm)	<10	<10	<10
Cr (ppm)	621 ± 44	897 ± 23	217 ± 14
Cu (ppm)	17 ± 1	38 ± 2	1750 ± 73
Fe (ppm)	4941 ± 314	7370 ± 77	3153 ± 124
Nb (ppm)	66 ± 6	189 ± 45	1102 ± 42
Ni (ppm)	377 ± 24	424 ± 6	361 ± 16
Ta (ppm)	377 ± 31	444 ± 3	466 ± 8
Ti (ppm)	82 ± 4	128 ± 4	399 ± 15
V (ppm)	33 ± 3	44 ± 3	112 ± 5
Zn (ppm)	37 ± 4	57 ± 8	79 ± 9
*S (wt%)	0.034 ± 0.26	0.03 ± 0.005	0.006 ± 0.001
Co (wt%)	5.95 ± 0.19	5.96 ± 0.11	6.04 ± 0.29
W (wt%)	87.7 ± 0.26	87.60 ± 0.26	87.93 ± 0.58
*C (wt%)	5.85 ± 0.07	5.81 ± 0.05	5.63 ± 0.02
Element	NP-prod	PRZ-prod	
Ca (ppm)	<10	<10	
Cr (ppm)	153 ± 1	184 ± 7	
Cu (ppm)	44 ± 2	84 ± 10	
Fe (ppm)	398 ± 48	1446 ± 58	
Nb (ppm)	82 ± 8	502 ± 24	
Ni (ppm)	316 ± 7	345 ± 11	
Ta (ppm)	377 ± 31	798 ± 26	
Ti (ppm)	131 ± 10	685 ± 22	
V (ppm)	74 ± 3	31 ± 2	
Zn (ppm)	94 ± 18	40 ± 2	
*S (wt%)	0.008 ± 0.001	0.04 ± 0.002	
Co (wt%)	5.62 ± 0.11	5.82 ± 0.18	
W (wt%)	87.3 ± 0.06	87.60 ± 0.26	
*C (wt%)	5.73 ± 0.09	5.84 ± 0.07	

4.5.2 X-ray diffraction

Powder X-ray diffraction was performed on all of the spray dried powders, as shown in Figure 4-16. Prominent WC and low intensity Co peaks were detected. The cobalt peaks were more clearly visible for the new powders, compared to the recycled powders, and specific peaks were not always clearly distinguishable when comparing the various patterns, despite the known cobalt content of each alloy, which was set at 6wt% for this research.

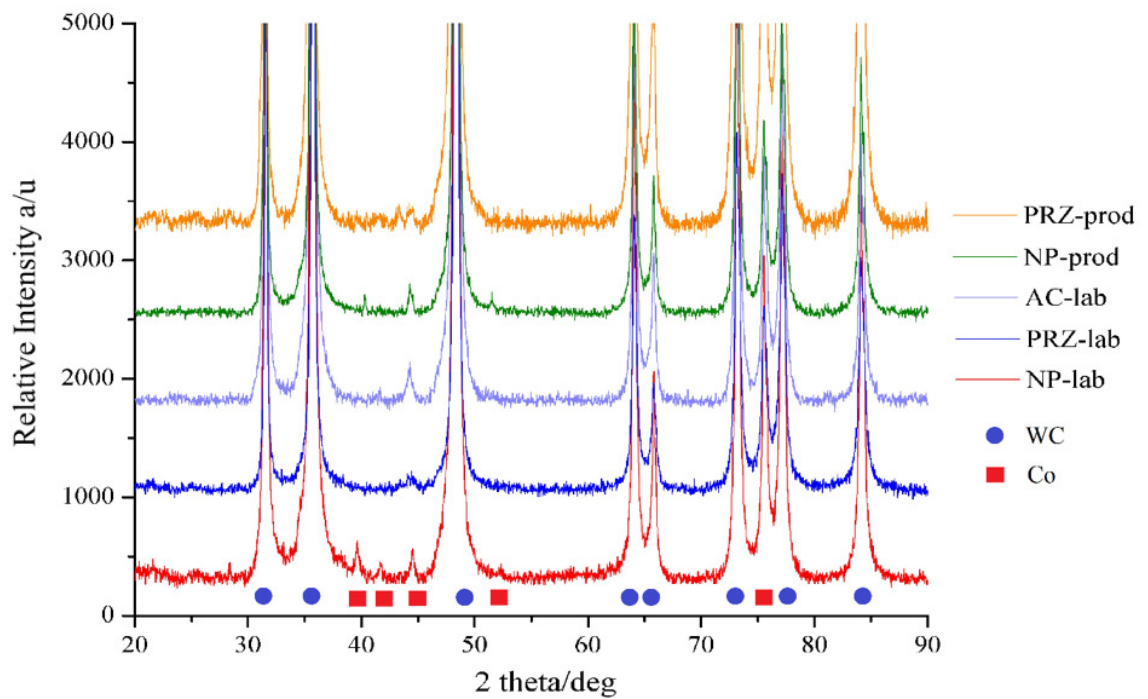


Figure 4-16 XRD patterns of the various spray-dried powders showing WC and Co peaks.

4.5.3 SEM and micro-PIXE

Figure 4-17 and 4-18 show typical SEM images with the corresponding W_L , Co and Fe micro-PIXE composition maps for each spray dried, polished powder. In the figures, the circular regions indicated on the W_L maps, designated by numbers

1 to 5 are regions of the powder granules from which micro-PIXE compositional data was extracted (refer to Table 6, p 92).

When comparing the Fe maps and the data listed in Table 6, Grade PRZ-lab showed the highest Fe levels, with lower levels detected in grade NP-lab, followed by AC-lab. A small amount of Fe was found in grade PRZ-prod and very little in NP-prod. In Table 6, some elements are listed as 'not detected'. This does not mean that the elements were not present in these grades; rather the region of the powder granule from which the micro-PIXE data was extracted did not contain these elements or the concentration was below the minimum detection limit. The data in Table 6 indicates that individual powder granules contained a variety of impurities of varying levels with Fe being the dominant impurity. Zinc was not detected in any of the powders, indicating that it was successfully extracted from the recycled materials. Other minor impurities included Ni and Cr (from milling in stainless steel mills) and Ti. Copper and sulphur were detected, but are constituents of the thermosetting resin used to mount the samples, and not the powders themselves.

The W_L and Co maps (Figure 4-17 and 4-18) indicate that the distribution of each phase, within the powder granules for each grade, was not homogeneous for all of the grades. Cobalt was better distributed in the recycled grades (PRZ-lab, AC-lab and PRZ-prod) than in the new grades (NP-lab and NP-prod). This was confirmed with SEM images taken at a higher magnification with corresponding W_L, Co and Fe micro-PIXE composition maps as shown in Figure 4-19 and 4-20 (p 93 - 94). Large Co agglomerates were clearly identified in grade NP-lab and NP-prod and to a lesser extent in grade PRZ-lab, AC-lab and PRZ-prod; which indicates inferior mixing and powder homogeneity between the new powders compared to the recycled powders. The Co and W distribution in grade PRZ-prod is more homogenous than all the other grades.

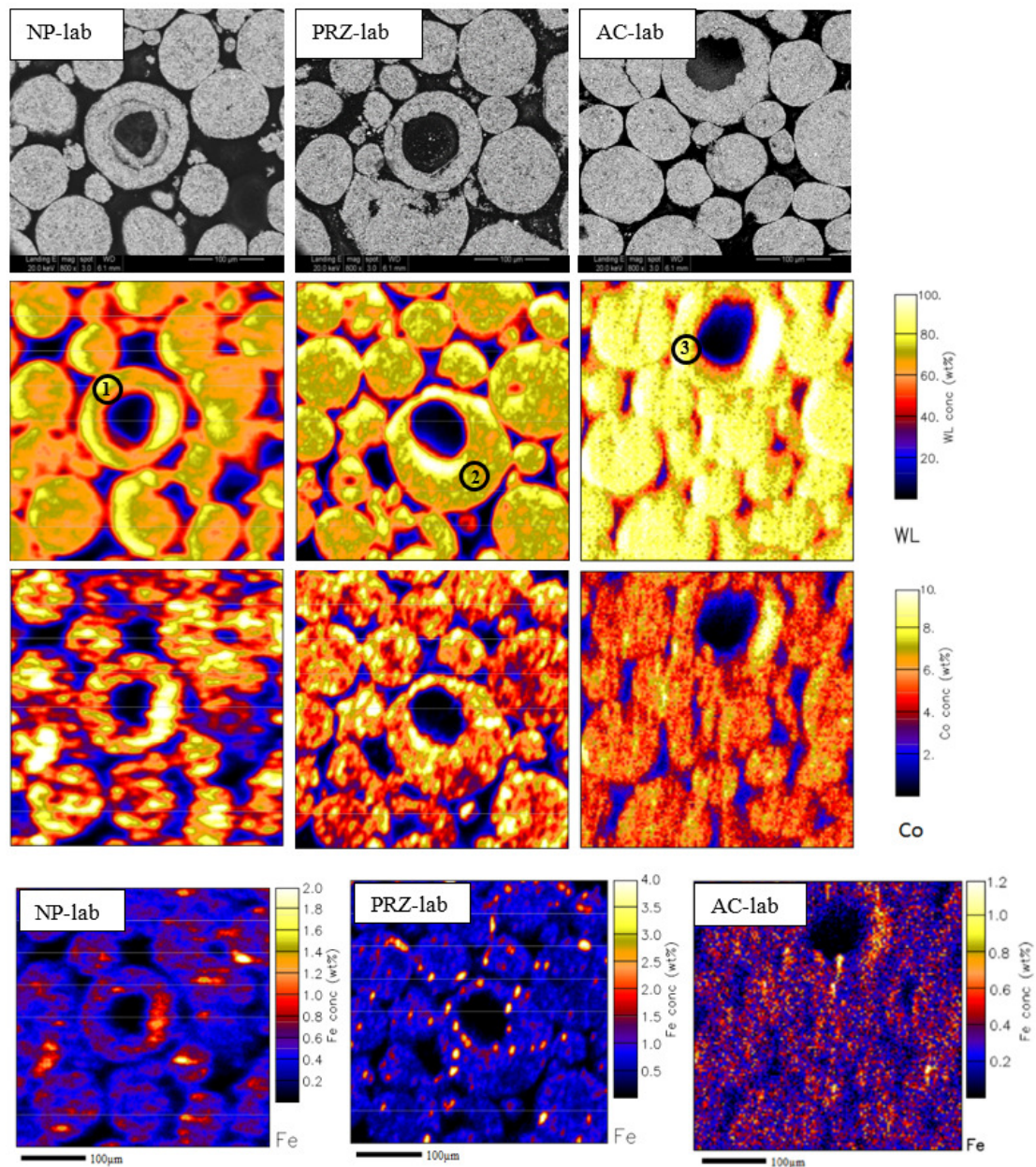


Figure 4-17 Granulated and polished powders of NP-lab, PRZ-lab and AC-lab showing SEM micrographs taken at 800x magnification in backscatter mode, the tungsten 'L' (WL), Co and Fe micro-PIXE maps. Areas 1, 2 and 3 are regions from which full elemental contributions were extracted for Table 6.

**Note: Fe concentration bars are not held constant due to varying intensities in the materials. Software and intensity limitations prevent constant scaling in this instance.*

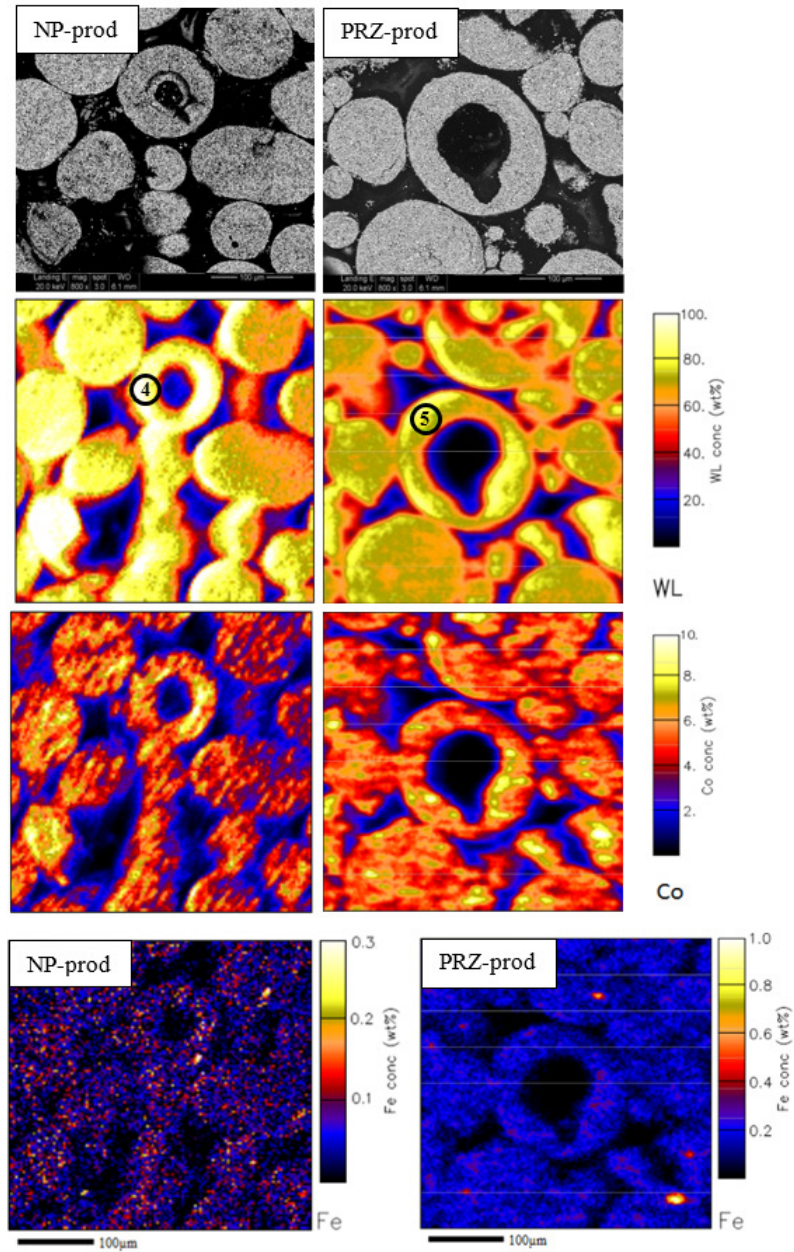


Figure 4-18 Granulated and polished powders of NP-prod and PRZ-prod showing SEM micrographs taken at 800x magnification in backscatter mode, the tungsten 'L' (WL), Co and Fe PIXE maps. Areas 4 and 5 are regions from which full elemental contributions were extracted for Table 6.

**Note: Fe concentration bars are not held constant due to varying intensities in the materials. Software and intensity limitations prevent constant scaling in this instance.*

Table 6: *Extracted micro-PIXE elemental compositions of localized areas (Figure 4-17 and 4-18: numbers 1-5) of WC-6wt% Co spray dried powder granules.*

Element	NP-lab	PRZ-lab	AC-lab	NP-prod	PRZ-prod
Ca (ppm)	582 ± 100 [182]	245 ± 64 [131]	< 377 ± 193 [377]	Not detected	393 ± 95 [182]
K (ppm)	499 ± 138 [234]	Not detected	Not detected	Not detected	Not detected
Cl (ppm)	849 ± 824 [502]	< 381	Not detected	< 715 ± 398 [715]	536 ± 474 [522]
Cr (ppm)	2102 ± 75 [96]	2365 ± 65 [70]	197 ± 109 [197]	< 128 ± 79 [128]	229 ± 68 [99]
Cu (ppm)	508 ± 1 [218]	202 ± 69 [159]	736 ± 199 [424]	1300 ± 170 [276]	1190 ± 115 [224]
Fe (ppm)	7336 ± 220 [94]	8117 ± 104 [69]	3500 ± 208 [184]	317 ± 85 [118]	2077 ± 97 [92]
Nb (ppm)	Not detected	Not detected	Not detected	Not detected	Not detected
Ni (ppm)	Not detected	1104 ± 95 [148]	1100 ± 283 [338]	243 ± 201 [221]	897 ± 193 [197]
Ta (ppm)	Not detected	Not detected	Not detected	Not detected	Not detected
Ti (ppm)	< 127	< 96	< 274 ± 149 [274]	Not detected	1317 ± 84 [134]
V (ppm)	Not detected	Not detected	Not detected	Not detected	Not detected
Zn (ppm)	Not detected	Not detected	Not detected	Not detected	Not detected
S (wt%)	1.30 ± 0.11 [0.09]	0.86 ± 0.04 [0.07]	1.1 ± 0.10 [0.20]	1.04 ± 0.99 [0.10]	1.23 ± 0.11 [0.09]
Co (wt%)	7.56 ± 0.01 [116 ppm]	5.31 ± 0.01 [68 ppm]	6.91 ± 0.78 [178 ppm]	7.27 ± 0.59 [113 ppm]	6.66 ± 0.01 [113 ppm]
W (wt%)	89.58 ± 1.08 [0.05]	68.13 ± 1.34 [0.04]	82.60 ± 0.40 [0.10]	80.30 ± 0.30 [0.69]	89.77 ± 1.08 [0.05]

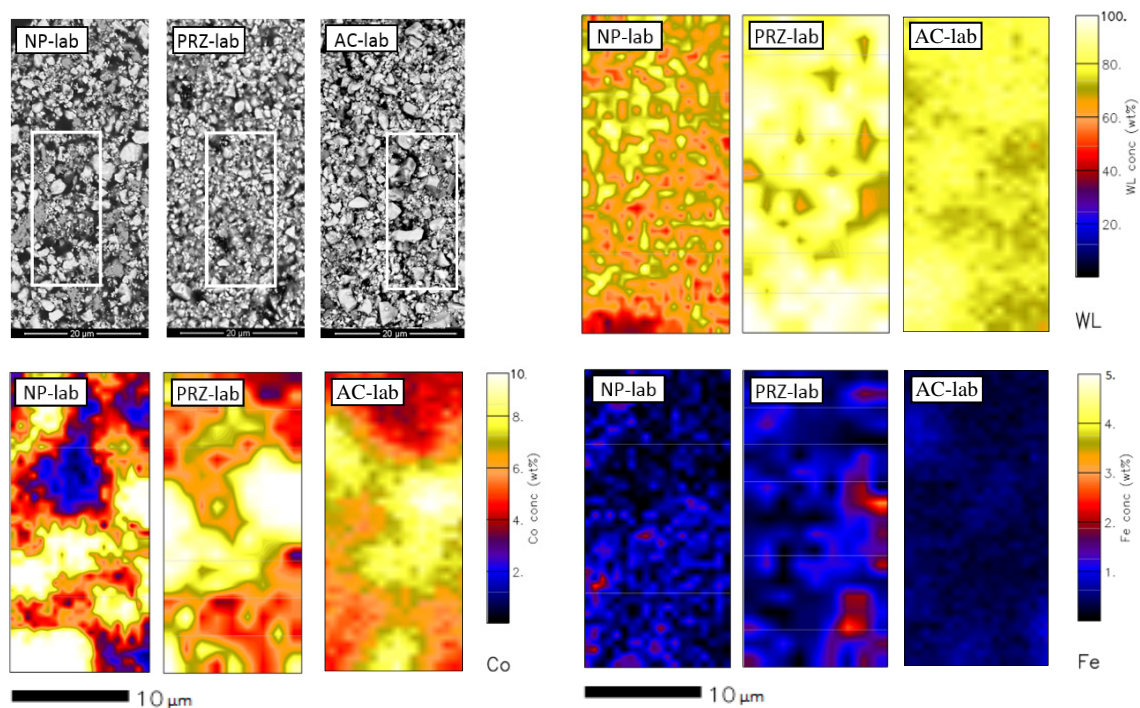


Figure 4-19 Zoomed in SEM micrographs taken at 5000x magnification in backscatter mode & grouped micro-PIXE maps: tungsten 'L' (W_L), Co and Fe micro-PIXE maps are shown for the laboratory milled powders.

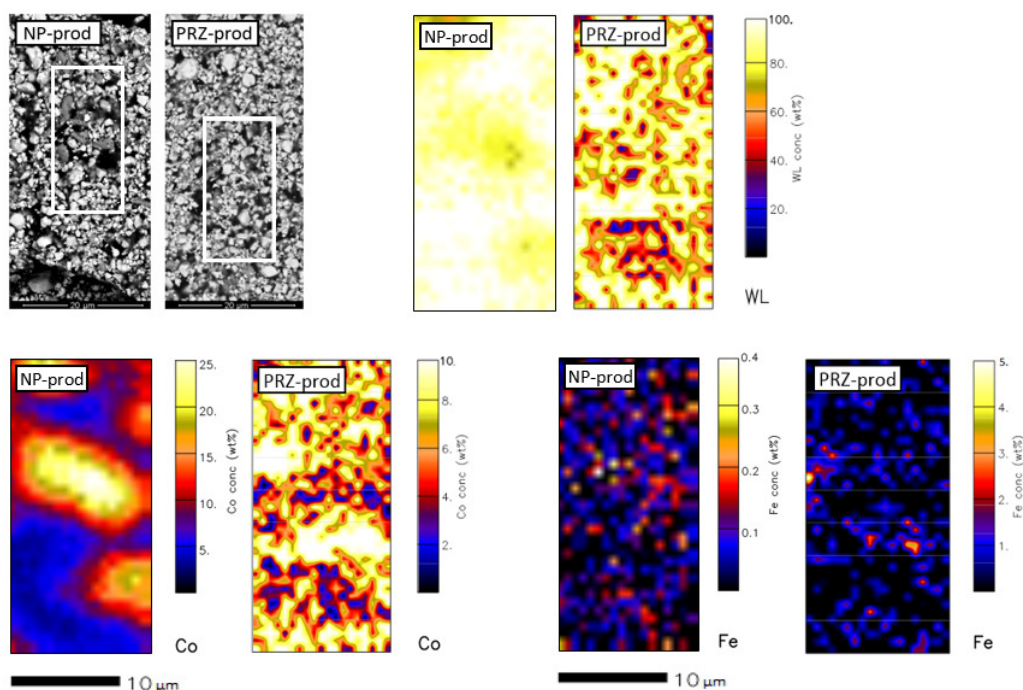


Figure 4-20 Production milled powders: SEM micrographs (5000X) and micro-PIXE maps, as for Figure 4-19. NP-prod Co and Fe scale bars were different from the other powders and hence have been shown separately.

4.5.4 Powder milling rates

Milling curves for powders composed of 100% AC, NP and PRZ materials were generated in a benchtop test mill (2 litre volume, which typically accommodates 2kg of powder) and are shown in Figures 4-21 and 4-22. This was done because production scale mills can be difficult to extract samples from, at regular intervals. Figure 4-21 shows the actual measured particle size of each powder during the full milling time. Figure 4-22 shows offset data, in which the powder graphs have been plotted where each powder particle size started between 3.2 and 3.4 μm. In this way, the different milling rates can be better compared from a similar starting particle size range.

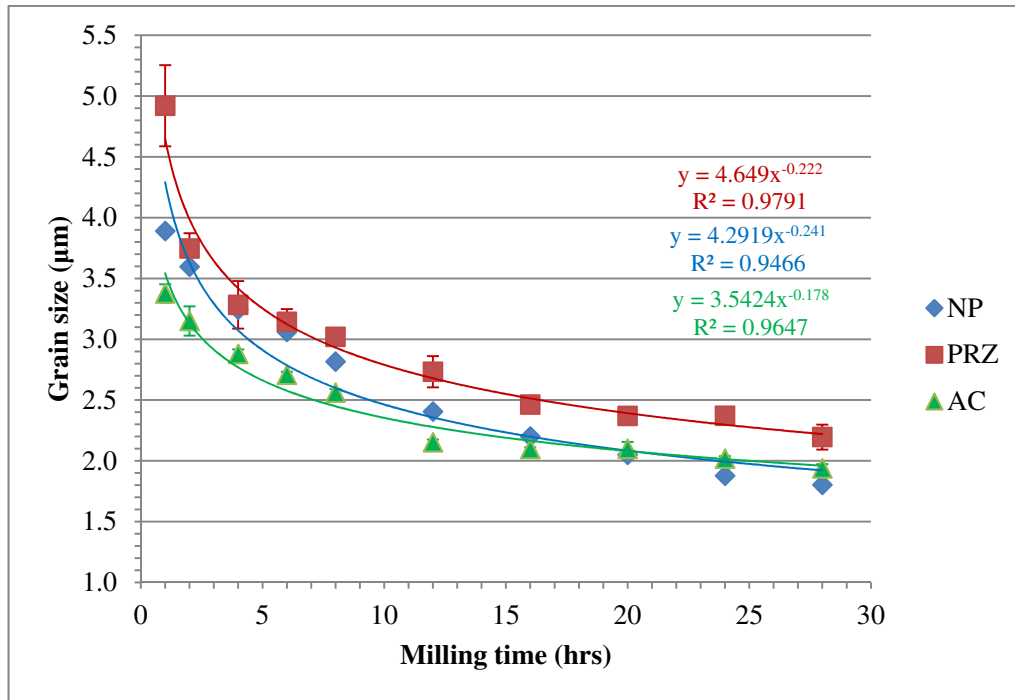


Figure 4-21 Actual milling curves of 100% NP, PRZ and AC powders as milled in a benchtop test mill.

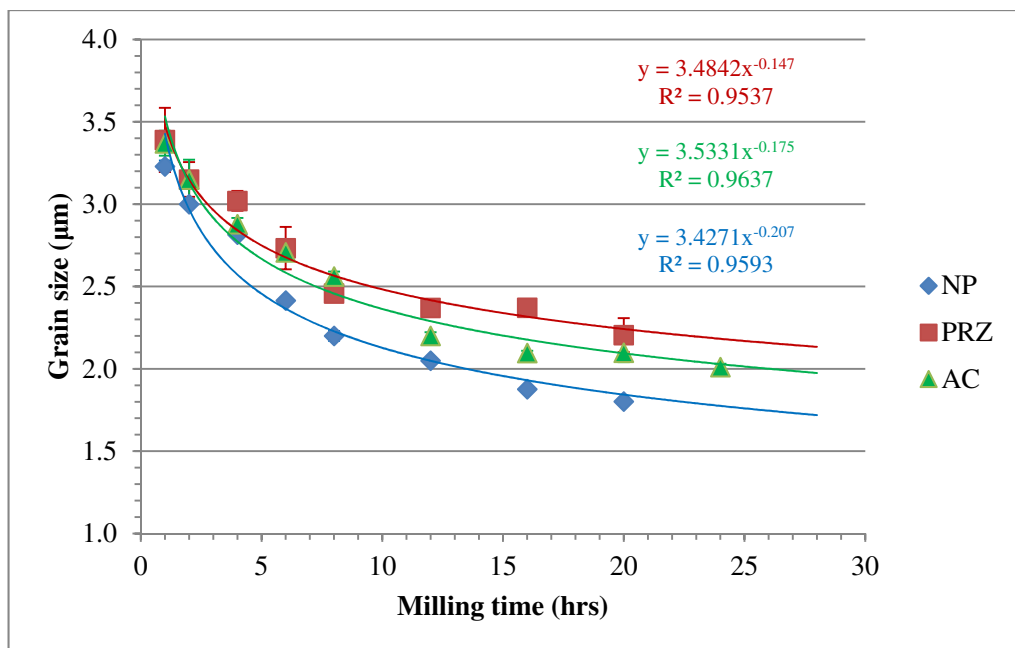


Figure 4-22 Offset milling curves of 100% NP, PRZ and AC powders, offset to a starting value of between 3.2 and $3.4\mu\text{m}$ to allow for a clearer appreciation of the different milling rates.

The milling curves show that PRZ material milled more slowly than AC material, and both recycled materials milled much more slowly than NP material, which achieved an offset particle size (Figure 4-22) below 2 μ m 11 hours faster than AC material, and according to the projected trend line, PRZ material would only reach 2 μ m after approximately 30 hours of milling.

SEM micrographs of the new (as-synthesized) starting powders used to manufacture the NP material, as well as the PRZ and AC starting powder (after the recycling process had completed) are shown in Figure 4-23 in which the new 4 μ m WC and Co powders had a very rounded morphology, while the PRZ and AC starting powders were angular, with WC-Co fused agglomerates evident in the PRZ material, and both very large and very fine particles were evident in the AC powder. Figure 4-24 and 4-25 (p 98 – 99) show the particle breakdown of the 100% NP, PRZ and AC powders over 28 hours of milling.

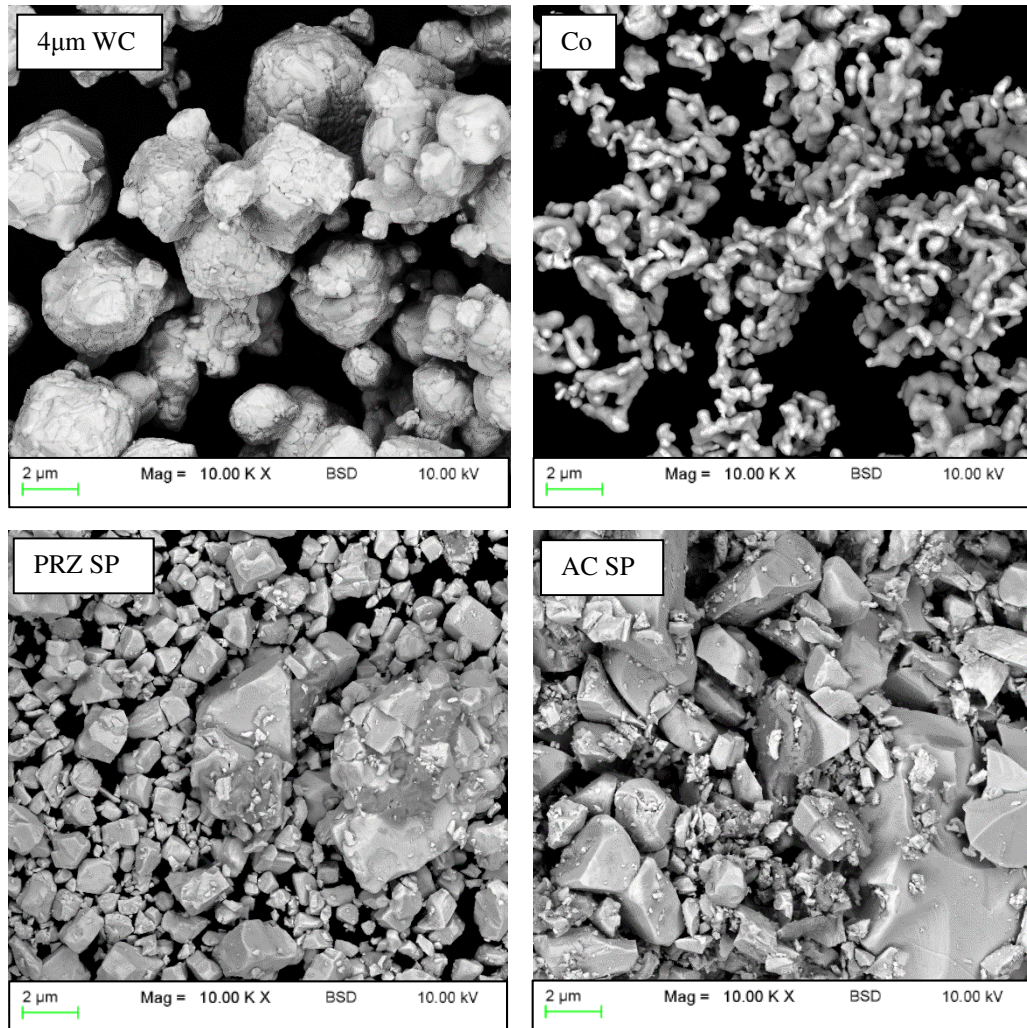


Figure 4-23 SEM micrographs taken at 10000X magnification, of the starting powders used to manufacture NP, PRZ and AC materials. The 4μm WC powder shows a rounded morphology, the cobalt powder shows a finely divided interwoven mesh of Co particles, and the AC and PRZ powders show a mixture of remaining sintered cobalt and angular WC grains across a wide particle size distribution.

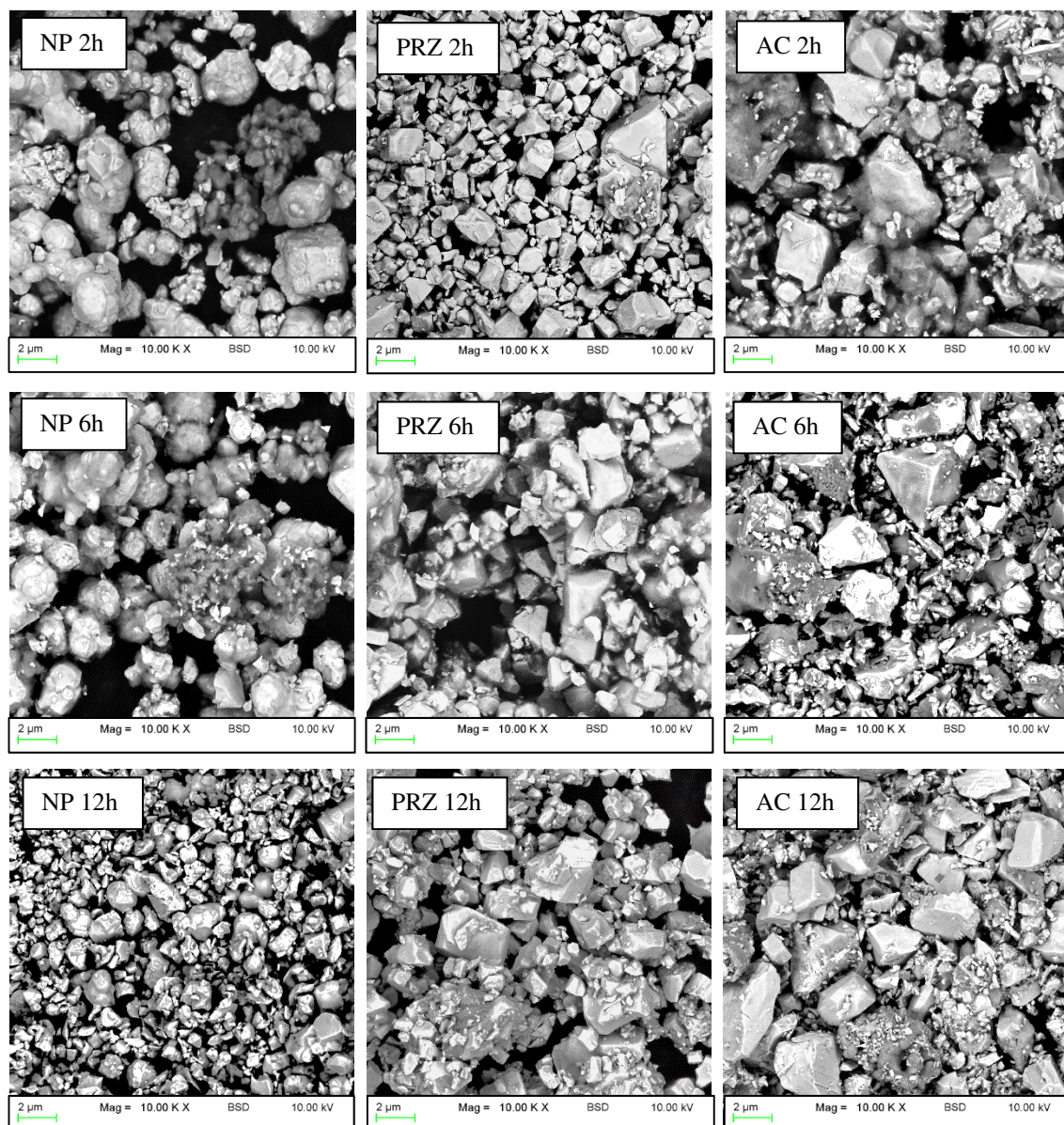


Figure 4-24 SEM micrographs taken at 10000X magnification showing the particle breakdown of 100% NP, PRZ and AC powders at 2h, 6h and 12h time intervals, extracted from a 2l test mill.

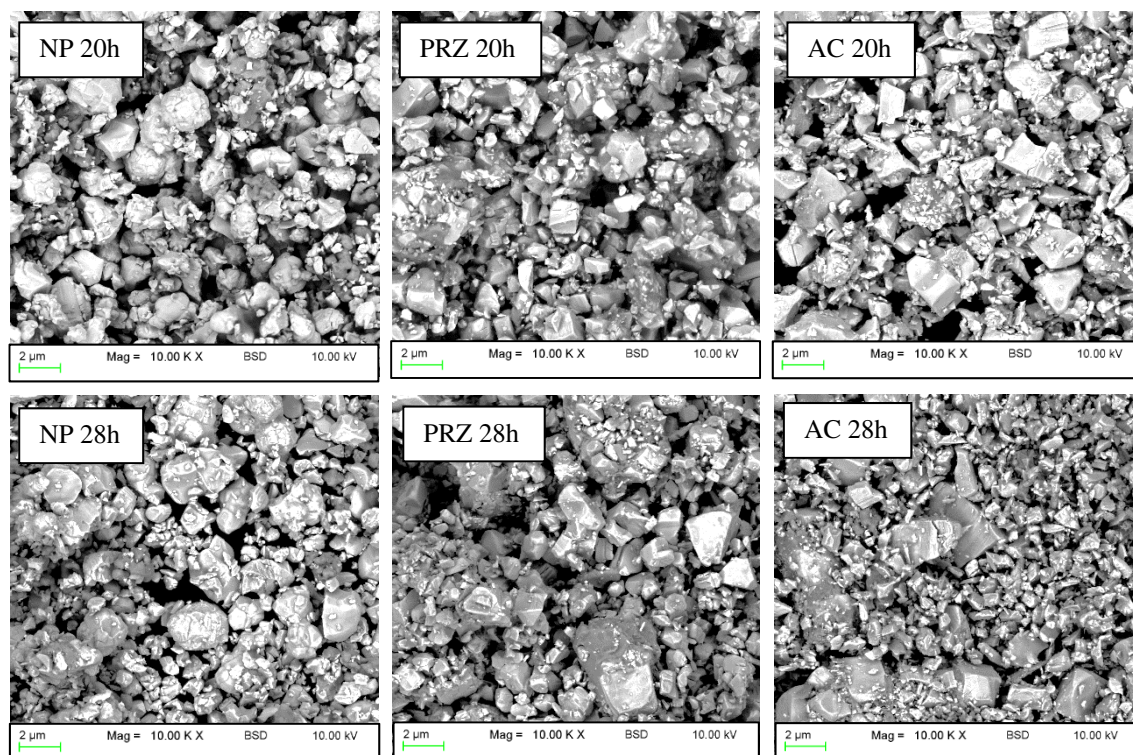


Figure 4-25 SEM micrographs taken at 10000X magnification showing the particle breakdown of 100% NP, PRZ and AC powders at 20h and 28h time intervals, extracted from a 2l test mill.

Even after 28 hours of milling, the rounded morphology of the NP powder was still evident, however the particle size was reduced and intermixed with cobalt. The PRZ material still showed some fused WC-Co grains that did not break down, but possessed a more even (narrower) particle size distribution than the AC material, which had some very large particles ($>10\mu\text{m}$) still present, as well as very fine particles. The SEM micrographs confirm the laser diffraction particle size measurements, showing that NP powders milled more quickly than the PRZ and AC powders, and possessed a narrower final particle size distribution.

4.5.5 Spray dried powder properties

The micro-PIXE results displayed earlier in this chapter were conducted on spray dried powders, but deal primarily with powder chemical composition, hence are

dealt with in that section. This section focuses on presenting particle sizes, microstructures and general powder characterization results. Powder rheology is presented later in its own chapter, because of its complexity.

4.5.5.1 Granule size distribution

In order to closely compare the spray dried powder properties and to facilitate meaningful powder rheology measurements, the powders were screened into 45-63 μ m, 90-125 μ m and 150-180 μ m particle size ranges. The screening process eliminates variations within the powder bulk (which include settling and agglomeration effects) which are generated by powder handling, movement, particle breakdown and storage.

The average granule mean volume diameter (Mv), D10, D50 and D90 particle sizes of all of the powders studied in this work are presented with their associated errors in Table 7. The finest screen fractions (45-63 μ m) of NP-lab, PRZ-lab, AC-lab and PRZ-prod fell within 2 μ m of each other when comparing their Mv, D10, D50 and D90 size ranges. The NP-prod (45-63 μ m fraction), however, possessed a coarser 45-63 μ m particle size distribution, most notably with a D10 value of 36.41 μ m, compared to a D10 of less than 5 μ m for the other powders. The humidified powders (NP-lab 45-63 H and PRZ-lab 45-63 H) were the same powders as NP-lab and PRZ-lab (45-63 μ m) and hence had the same particle sizes. The 90-125 μ m screen fraction particle size distributions were similar for all powders, but PRZ-prod had a slightly coarser overall particle size distribution of 5-10 μ m coarser than the other powders. Followed by AC-lab, which was 2 to 3 μ m finer than NP-prod, but coarser than the other powders. The 150-180 μ m screen fractions showed similar Mv results for the lab powders, and production powders, with the most notable difference being NP-Prod, which possessed the largest D10 value of 126 μ m compared to the second largest value of 119.70 μ m belonging to AC-lab, closely followed by PRZ-prod.

Table 7: Particle size distributions of each powder screen fraction in micrometres.

Powder	Mv	D10	D50	D90
PRZ-prod 45-63	45.22 ± 0.40	3.14 ± 0.36	47.94 ± 0.23	70.43 ± 1.87
NP-lab 45-63	45.44 ± 1.68	3.16 ± 0.33	48.79 ± 0.94	71.22 ± 3.47
NP-lab 45-63 H*	45.44 ± 1.68	3.16 ± 0.33	48.79 ± 0.94	71.22 ± 3.47
AC-lab 45-63	45.45 ± 3.61	3.31 ± 1.35	48.78 ± 2.82	70.35 ± 1.73
PRZ-lab 45-63 H*	46.66 ± 0.17	4.99 ± 0.65	48.87 ± 0.23	70.06 ± 0.31
PRZ-lab 45-63	46.66 ± 0.17	4.99 ± 0.65	48.87 ± 0.23	70.06 ± 0.31
NP-prod 45-63	52.47 ± 0.72	36.41 ± 0.82	53.15 ± 0.50	72.34 ± 1.05
NP-lab 90-125	104.67 ± 0.61	78.10 ± 0.34	101.20 ± 0.30	135.83 ± 2..37
PRZ-lab 90-125	107.53 ± 0.70	80.60 ± 0.08	103.33 ± 0.32	139.83 ± 1.72
NP-prod 90-125	106.73 ± 1.42	82.34 ± 0.83	103.17 ± 0.55	135.57 ± 4.41
AC-lab 90-125	112.13 ± 1.12	86.37 ± 0.45	108.63 ± 0.81	142.80 ± 2.35
PRZ-prod 90-125	114.43 ± 0.78	88.82 ± 0.30	111.40 ± 0.26	144.60 ± 2.21
NP-lab 150-180	152.93 ± 1.32	106.97 ± 3.46	149.33 ± 1.85	205.30 ± 6.32
PRZ-lab 150-180	153.70 ± 2.18	113.20 ± 2.51	150.57 ± 1.72	200.57 ± 2.03
AC-lab 150-180	157.57 ± 1.12	119.70 ± 4.10	153.50 ± 2.00	201.4 ± 12.32
NP-prod 150-180	164.93 ± 2.46	126.50 ± 0.52	160.60 ± 1.08	209.13 ± 7.03
PRZ-prod 150-180	167.63 ± 7.51	119.20 ± 6.32	157.43 ± 2.80	209.40 ± 1.13

* 'H' refers to powders exposed to 75% relative humidity for 24h. They were used to confirm the sensitivity of the powder rheometer when measuring spray dried powders.

4.5.5.2 Granule microstructures and morphology

Scanning electron micrographs of the 150-180µm and 45-63µm screen fractions of each powder are shown in Figures 4-26 (p 103) and 4-27 (p 104) respectively. Primarily solid granules with only small internal voids, if present at all, belonged to NP-Prod (Figure 4-26). PRZ-prod, NP-lab, and PRZ-lab (Figure 4-26) contained a number of cracked granules, with the cracks intersecting the large internal voids. The wall thickness of the granules was variable because of the position of the internal void, where NP-prod (Figure 4-26) possessed smaller, more centrally located internal voids, if present. NP-prod possessed more spherical granules, of uniform size, and fewer irregular and broken granules compared to PRZ-prod, NP-lab, and PRZ-lab. AC-lab had almost completely solid granules,

displaying small internal voids and a less densely packed structure. The finer powders of the 45-63 μ m screen fractions (Figure 4-27), displayed a similar trend, with hollow granules visible for PRZ-prod, NP-lab, AC-lab and PRZ-lab and more broken and irregular granules were observed in these powders compared to NP-prod (Figure 4-27) which had more spherical, solid, uniformly sized granules. Optical micrographs of the external appearance of the 45-63 μ m granules are shown in Figure 4-28 (p 105). PRZ-prod had fine dust particles adhering to the granules, as did AC-lab, while the other powders (NP-prod, NP-lab and PRZ-lab) did not display this effect and had smoother granule surfaces. Spherical granules of a uniform size distribution can be seen for NP-prod (Figure 4-28, p 105), where the other powders had some irregularly shaped granules as well as some fine particles within their particle distribution.

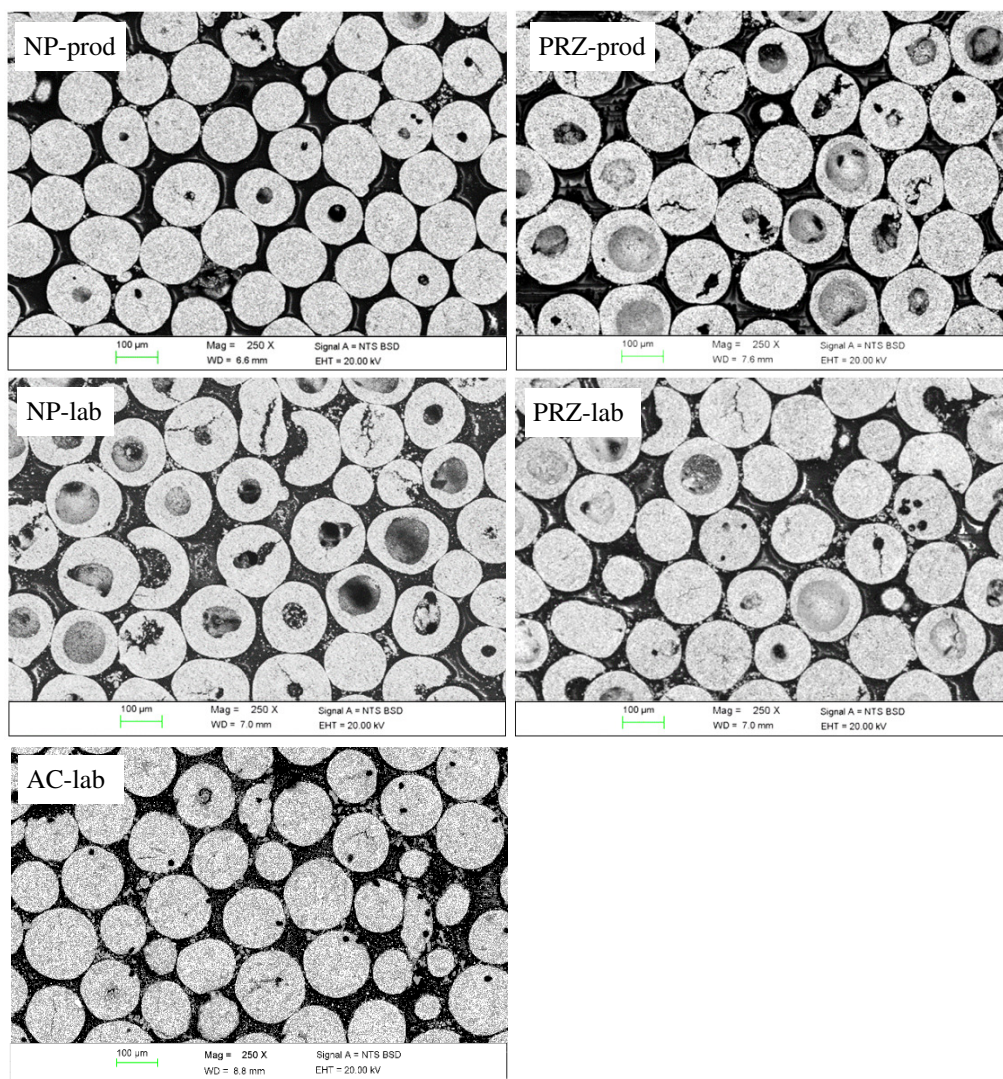


Figure 4-26 Scanning electron micrographs of the 150-180µm powder screen fractions at 250X magnification in backscatter mode.

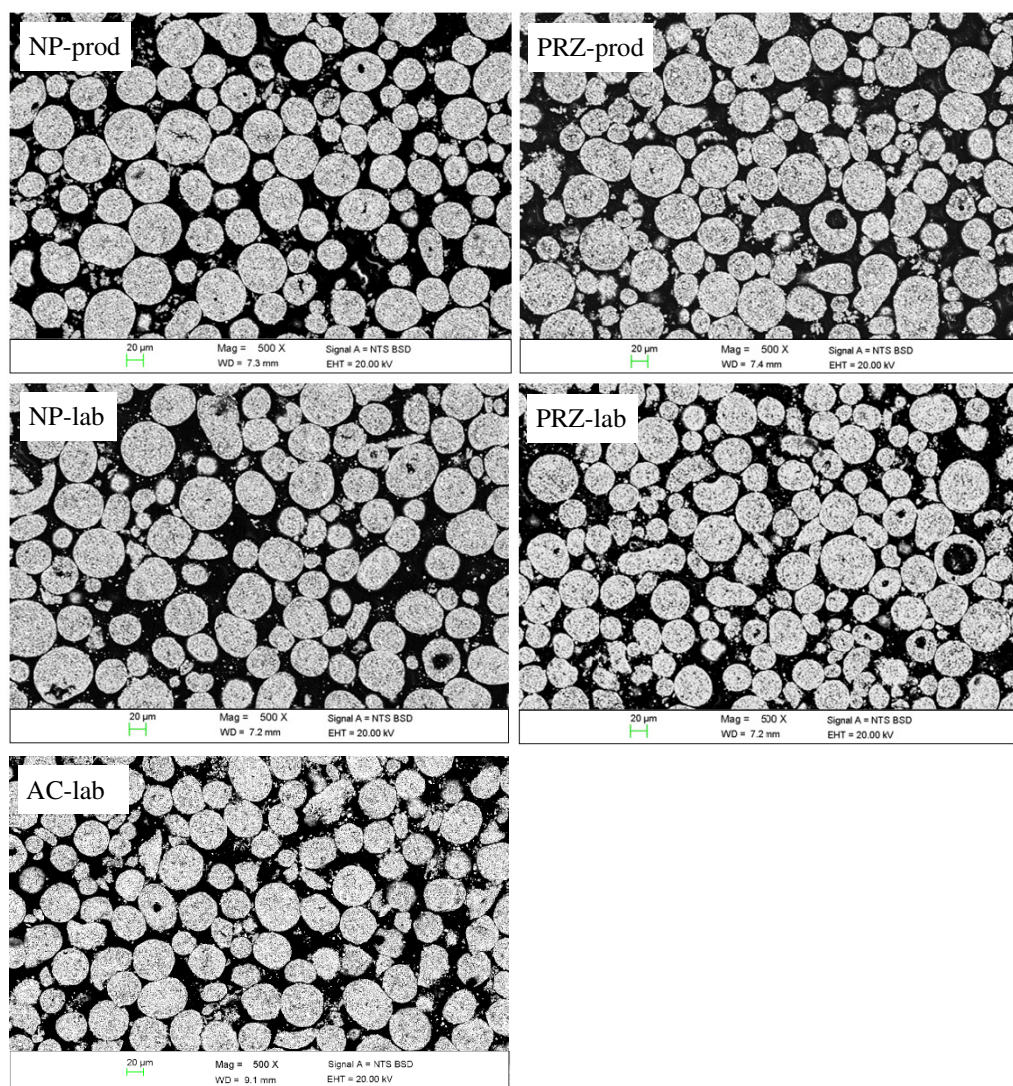


Figure 4-27 Scanning electron micrographs of the 45-63 μ m powder screen fractions at 500X magnification in backscatter mode.

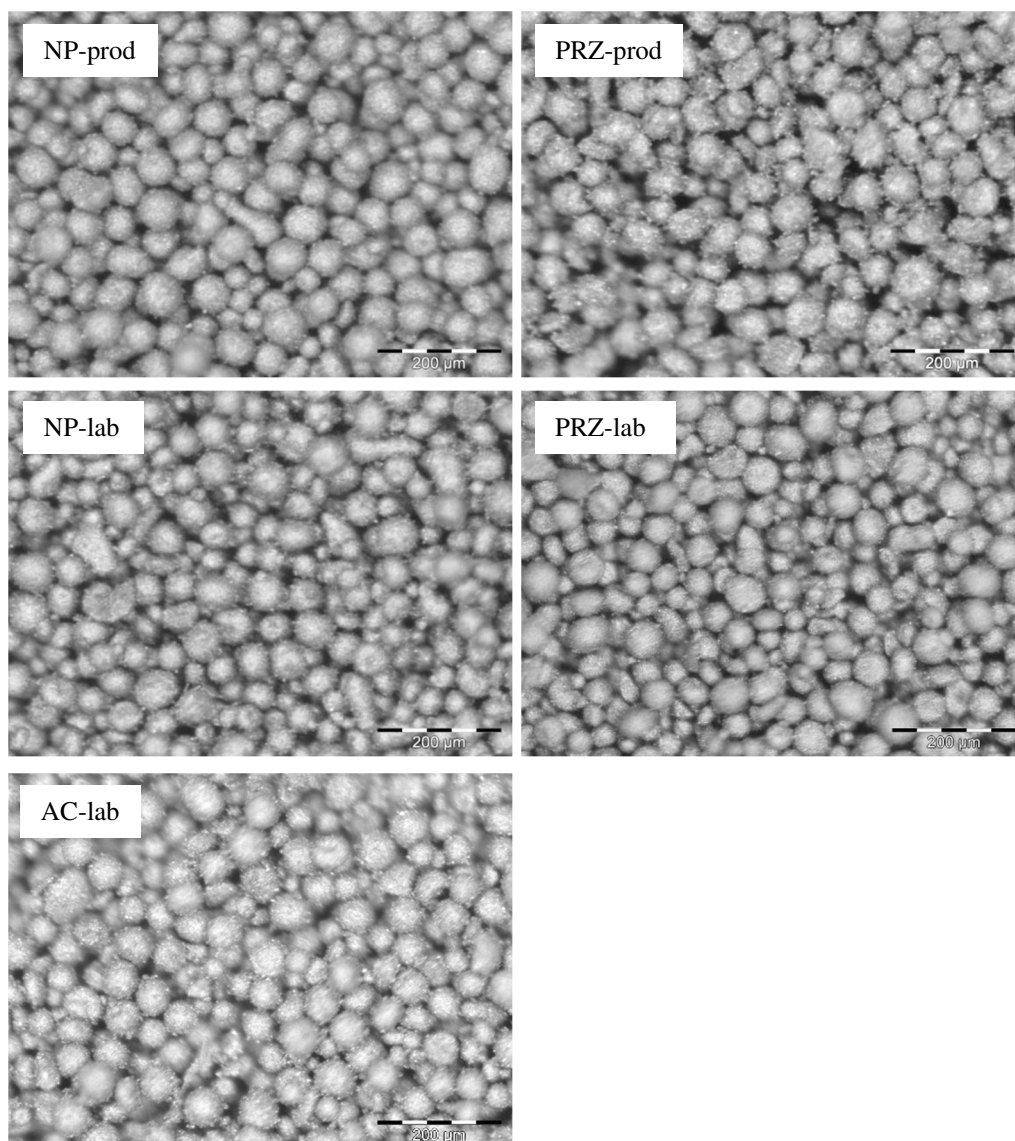


Figure 4-28 Optical micrographs of the 45-63 μ m powder screen fractions of NP-prod, PRZ-prod, NP-lab, PRZ-lab at 80X magnification, showing the external powder morphologies.

4.5.5.3 Apparent density and flow rate

Figure 4-29 A and B show the apparent density and flow rate of the various screen fractions of the powders. PRZ-prod had the lowest density in the 45-63 μ m fraction (Figure 4-29 A) and the highest flow time (Figure 4-29 B). PRZ-prod 45-63 μ m powder was highly cohesive and experienced flow difficulties, hence the large error in its flow rate. NP-lab and PRZ-lab had very similar densities and flow times for most of the apparent density and flow rate measurements. Aside from the flow problems and low density of the 45-63 μ m fraction, PRZ-prod followed a similar trend to NP-lab and PRZ-lab across the measurement range. That is, from the 63-90 μ m fraction up to the largest fraction (180-212 μ m), the powders NP-lab, PRZ-lab and PRZ-prod decreased in apparent density with each increasing size fraction and correspondingly increased their flow time the same way. AC-lab behaved similarly to NP-prod, however it possessed a consistently lower apparent density than the other powders across all screen fractions and like PRZ-prod, it experienced a high flow time for the 45-63 μ m screen fraction.

By comparing the screen fraction with the highest apparent density i.e. the 63-90 μ m fraction in the case of NP-lab and PRZ-lab, with the 180-212 μ m fraction, which had the lowest apparent density, PRZ-lab and NP-lab experienced a maximum difference in density of 0.5 to 0.6 g/cc. PRZ-prod varied by 0.4-0.5g/cc with its maximum apparent density at the 90-125 μ m screen fraction and its minimum at the 180-212 μ m fraction. A similar trend occurred with AC-lab, however its maximum density (and conversely lowest flow time) occurred at the 63-90 μ m screen fraction. NP-prod, however, only varied by up to 0.15g/cc in density, with its maximum at the 90-125 μ m fraction and its minimum at the 180-212 fraction. NP-prod also experienced the fastest flowing powder in every screen fraction measurement (Figure 4-29 B) with least fluctuation between different sized powders.

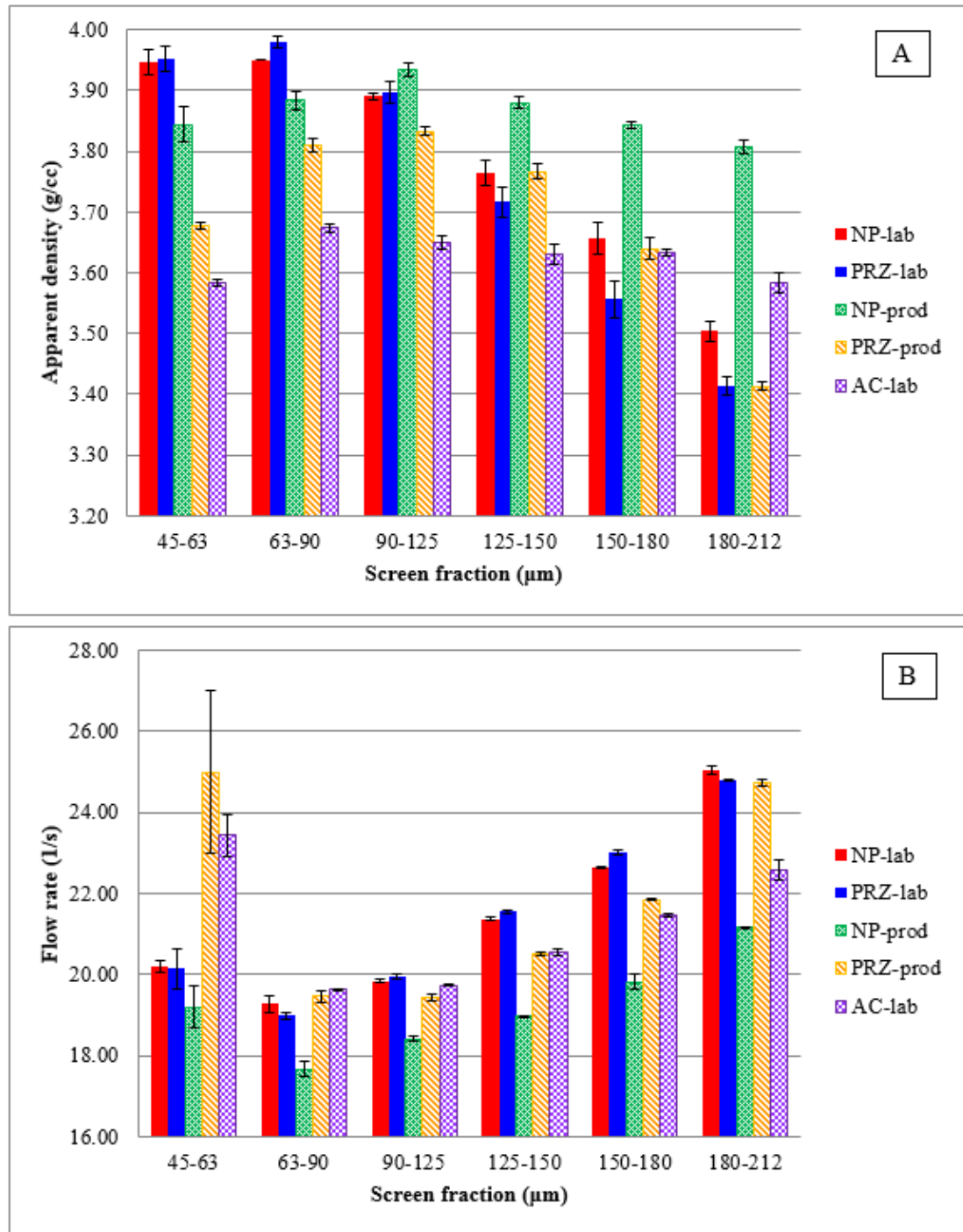


Figure 4-29 Apparent density (A) and flow rate (B) of the new and recycled powders, displaying six screen fractions ranging from 45μm up to 212μm.

4.5.5.4 Powder compaction (pressing)

The results of the pressing tests of the laboratory milled powders are shown in Figure 4-30. Each test spanned a range of 6 data points, pressed from a high pressing force (at low shrinkage) that usually led to a cracked component, to a low force (and high shrinkage) and an unsuitably soft component that could readily break apart. The PRZ-lab and NP-lab powders pressed almost identically at each shrinkage value. All points, except the 17% shrinkage, overlapped. However, the AC powder consistently required a greater force for compaction at each shrinkage value. Because of this, it was also tested across a broader range, up to 26% shrinkage, to better observe its behaviour at higher shrinkage values. The exponential curves of the other two powders were extrapolated forward to compare with the AC curve. The AC powder consistently required a higher compaction force at each shrinkage value, and displayed fewer cracks across the entire shrinkage range tested than NP-lab and PRZ-lab, which cracked at both their lowest and highest tested pressing shrinkages. The trend lines and equations of each curve demonstrate a near perfect exponential fit to the data (with an R^2 value very close to 1).

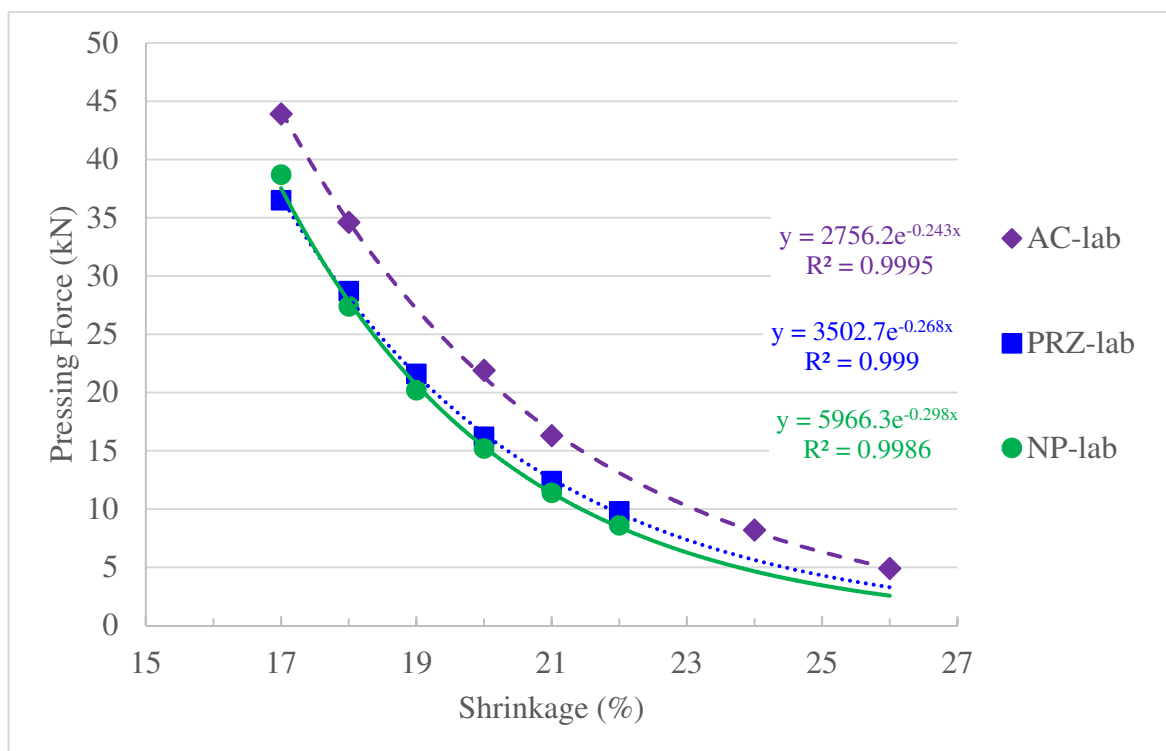


Figure 4-30 Pressing force against % shrinkage for the laboratory milled powders: new powder (NP-lab), zinc recycled powder (PRZ-lab) and the acetic acid powder (AC-lab), with their associated exponential equations.

4.6 Slurry rheology

Slurry rheology results are presented in this section. Other analyses that directly impact slurry rheology have also been included here. The section begins with the effects of milling on the integrity of the added polymers, followed by zeta potential measurements, grain size effects and finally slurry rheology measurements.

4.6.1 Milling effects on the polymer additives

Slurry rheology is extremely sensitive to small changes in composition of the slurry, and directly impacts the quality of the spray dried powders. It was therefore necessary to extract the polymers to measure if there was an impact on their molecular weight due to milling.

The number average (M_n) and weight average (M_w) molecular weights and polydispersity indices (PDI) of the polymers extracted from the powders are shown in Table 8. The 'control' is the original binder (as supplied) before blending with the powder. The polymer extracted from the NP-lab powder has a lower M_n and M_w than that extracted from the PRZ-lab powder, despite being milled for a shorter time period. The polymers extracted from the NP-prod and PRZ-prod powders have very similar M_n and M_w values. PDI values for all the extracted polymers range between 1.21 and 1.27. The polymers showed no obvious breakdown in response to milling.

Table 8: *Molecular weights and polydispersivity indices of the polymer binder system.*

Powder batch	Mn (Daltons)	Mw (Daltons)	Polydispersivity index: PDI	Milling time** (hours)
Control	3383	4262	1.21	N/A
NP-lab	2865	3629	1.27	14
PRZ-lab	3042	3801	1.25	26
NP-Prod	3191	3969	1.24	4
PRZ-prod	3170	3884	1.23	4

* Control refers to the original polymer binder, in the same proportions as used in the milled powders, but without milling

**The number of hours the polymer binder system was exposed to milling

4.6.2 Particle size and zeta potential

It was necessary to determine the effects of variable particle size on slurry rheology, to properly characterize the slurry flow behavior. Hence, various additional test powders (of composition WC-6wt% Co) were produced from starting material of varying sizes. These have been designated according to their particle size (WC-1.3 μ m to WC-4.1 μ m) in Table 9 which shows the particle size distribution of each slurry. The particle size range of the additional ‘WC’ powders span the entire particle size range of the materials produced in this study. Zeta potential values are shown in Table 10.

Despite attempts to mill PRZ-lab, NP-lab, PRZ-prod and NP-prod to the similar target grain size distributions, different milling rates were observed. Hence NP-prod-remill was produced to better correlate with the PRZ prod (which was coarser than the other grades), to compare their behaviour when the grain sizes are the same. PRZ-prod and NP-prod-remill possessed Mv grain size values within 0.1 μ m of each other. NP-lab and NP-prod were approximately 0.5 microns finer than PRZ-lab and PRZ-prod respectively.

Table 9 Grain size distributions of the various slurries.

Powder batch	Mv (μm)	D10 (μm)	D50 (μm)	D90 (μm)
NP-lab	1.357 ± 0.003	0.459 ± 0.001	1.076 ± 0.003	2.585 ± 0.007
PRZ-lab	1.869 ± 0.001	0.990 ± 0.012	1.811 ± 0.004	2.824 ± 0.009
AC-lab	1.656 ± 0.348	0.416 ± 0.061	1.224 ± 0.078	3.310 ± 0.334
NP-prod	1.431 ± 0.004	0.534 ± 0.002	1.230 ± 0.002	2.596 ± 0.006
PRZ-prod	1.897 ± 0.007	0.478 ± 0.004	1.578 ± 0.013	3.790 ± 0.010
NP-prod-remill	1.926 ± 0.004	0.645 ± 0.001	1.661 ± 0.004	3.563 ± 0.006
WC-1.3μm	1.307 ± 0.011	0.548 ± 0.001	1.153 ± 0.005	2.277 ± 0.041
WC-1.4μm	1.386 ± 0.007	0.584 ± 0.001	1.135 ± 0.002	2.523 ± 0.014
WC-2.0μm	1.973 ± 0.003	0.719 ± 0.003	1.861 ± 0.003	3.323 ± 0.006
WC-2.9μm	2.893 ± 0.003	1.262 ± 0.003	2.751 ± 0.004	4.633 ± 0.006
WC-4.1μm	4.040 ± 0.017	1.895 ± 0.004	3.893 ± 0.021	6.353 ± 0.029

Table 10 Zeta potentials of the starting powders and milled powders.

Powder batch	Zeta Potential (mV)	Standard Deviation (mV)
Co (pure, 1.5 μ m)	+7.15	19.2
WC (pure, 1.8 μ m)	-5.21	23.6
PRZ powder*	-29.9	22.7
NP-lab	-4.6	14.4
PRZ-lab	-22.2	18.2
NP-prod	-0.4	18.4
PRZ-prod	-16.3	19.7
NP-prod-remill	-16.9	16.3
AC-lab	-19.5	19.7
WC-1.3 μ m	-37.6	15.3
WC-1.4 μ m	-14.3	16.5
WC-2.0 μ m	-34.9	19.2
WC-2.9 μ m	-9.6	19.9
WC-4.1 μ m	-19.9	18.1

* The starting powder before further PRZ milling i.e. powder extracted from the PRZ production process.

Comparing the particle sizes in Table 9 to the zeta potentials shown in Table 10, no clear correlation exists between these parameters. All the PRZ powders had a zeta potential greater than -16mV, including the original NP-lab recycled powder used to produce PRZ-lab, which possessed a zeta potential of -29.9mV. No PRZ material had a zeta potential close to zero, while new powders varied significantly, from values close to zero to approximately -30mV.

4.6.3 Slurry rheology measurements

4.6.3.1 Effect of particle size

The effect of grain size on the slurry shear stress as a function of shear rate is shown in Fig. 4-31, for the powders milled under high solids loading conditions i.e. using 11.89wt% ethanol (see Table 2, page 49). The decelerating curves have been omitted from the graph for clarity; there is a large overlap with the accelerating curves. The shear stress increases with decreasing particle size, indicating large inter-particle differences between the slurries. The particle size difference between powders WC-1.3 μm and WC-1.4 μm is only 0.1 μm , yet the maximum shear stress at 500s⁻¹ for WC-1.3 μm exceeds 170Pa, while that of WC-1.4 μm is 117Pa. The curves for powders WC-2.9 μm and WC-4.1 μm overlap, showing the lowest shear stress values, with a maximum of 25Pa, at a shear rate of 500s⁻¹. Powder WC-2.0 μm showed moderate shear stresses, with a maximum of approximately 40Pa.

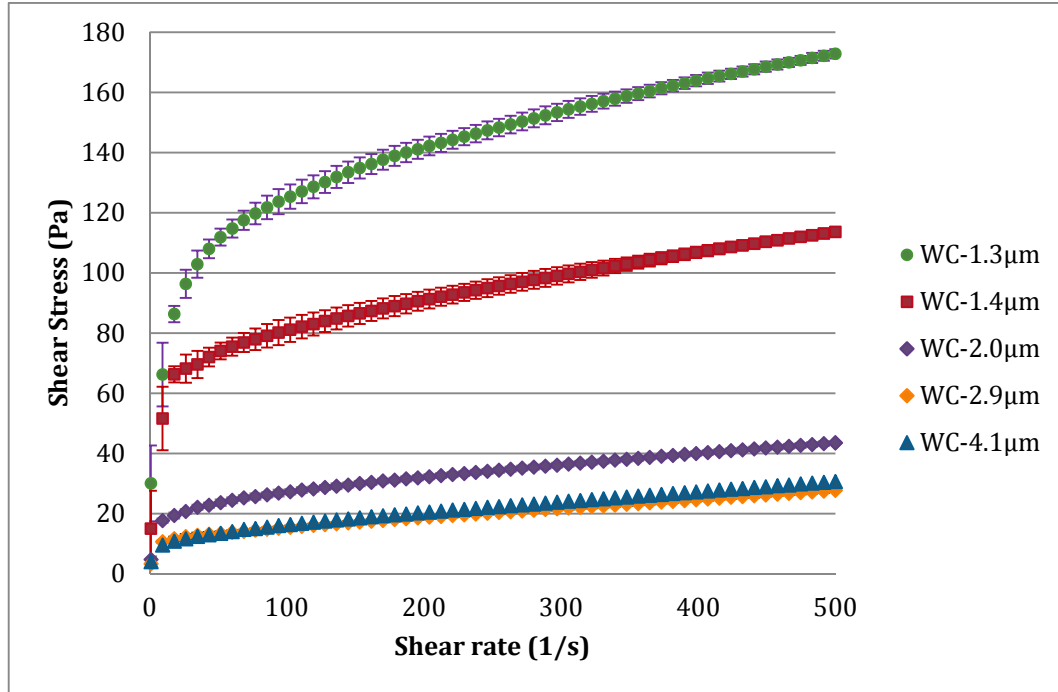


Figure 4-31 Shear stress against shear rate comparison (accelerating curves only for clarity) between experimentally milled WC-6wt% Co powders of different grain sizes.

SEM images of the powders are shown in Fig. 4-32, where the particle size differences are clearly visible. The Co binder is darker and more rounded in shape, with the WC grains visible as the light grey, generally angular shapes. The Co and WC are well distributed in each powder. The larger WC grains appear angular compared to the smaller WC grains, which seem more rounded.

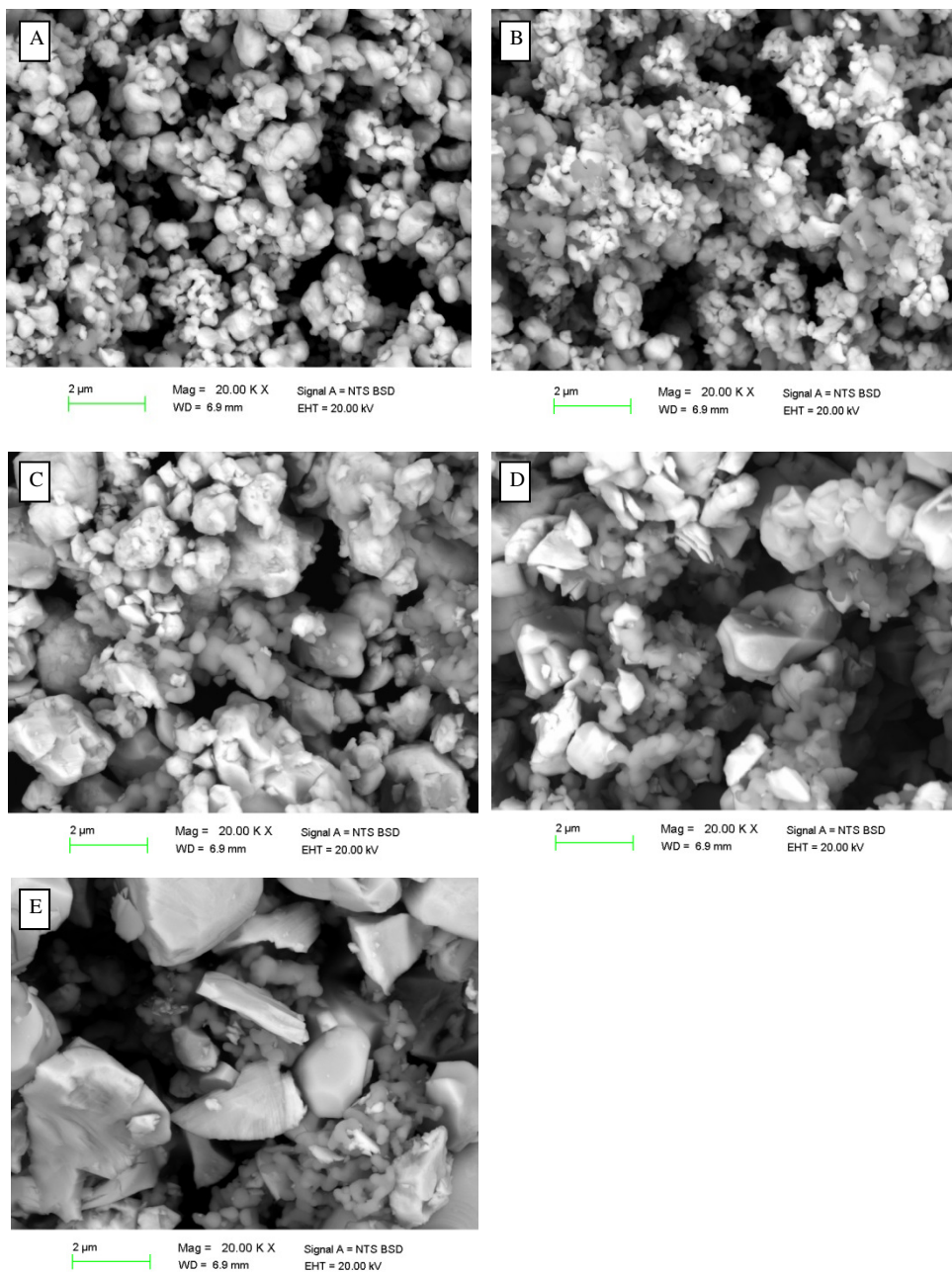


Figure 4-32 SEM micrographs of new WC powders (dried slurries) of the various size ranges in backscatter mode, at 20000X magnification. A: WC-1.3 μm , B: WC-1.4 μm , C: WC-2.0 μm , D: WC-2.9 μm , E: WC-4.1 μm .

4.6.3.2 New vs. recycled powders

Figure 4-33 shows the shear stress as a function of shear rate for the NP-lab, PRZ-lab, AC-lab, NP-prod and PRZ-prod powders.

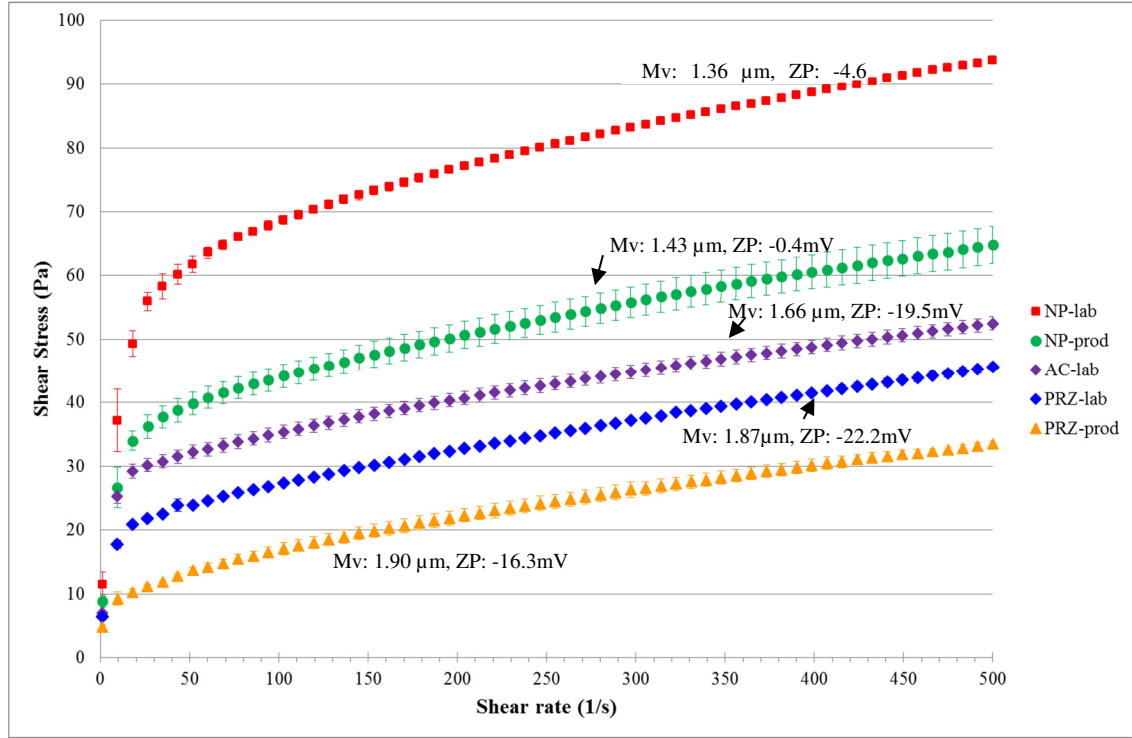


Figure 4-33 Shear stress against shear rate comparison between experimentally milled (lab) and production grade (prod) new and recycled WC-6% Co powders at 11.89wt% ethanol. Mv indicates the mean volume grain size, ZP indicates the zeta potential.

The mean volume grain size (Mv) and zeta potential (ZP) for each slurry is also shown. The accelerating and decelerating shear stress curves overlapped (decelerating curves omitted for clarity), indicating that none of the slurry viscosities changed markedly during measurement. The ranking order from highest to lowest shear stress as a function of shear rate is: NP-lab, NP-prod, AC-lab, PRZ-lab and PRZ-prod. The zinc recycled powders had lower shear stresses, a tendency for more negative zeta potentials, and coarser grains compared to the new powders, under both laboratory and production milling conditions. AC-lab

also had a negative zeta potential compared to the new powders and an Mv particle size between the zinc recycled and new powders. The laboratory milled powders had more negative zeta potentials than the production milled powders, for both the recycled and new powders.

The highest shear stress (at 500s^{-1} shear rate) of 93.7Pa, recorded for NP-lab, corresponds to the finest grain size of $1.36\mu\text{m}$ and a low (close to zero) zeta potential. The lowest shear stress of 33.5Pa, recorded for PRZ-prod, corresponds to the coarsest grain size of $1.90\mu\text{m}$ and a zeta potential of -16.3mV. SEM micrographs of the powders are shown in Fig. 4-34. NP-lab, NP-prod and NP-prod-remill showed a clear contrast between the WC grains (light grey) and the Co binder (dark grey). The contrast between the WC and Co phases was generally, not clearly distinguishable in the zinc recycled powders, as shown for PRZ-lab and PRZ-prod. The acetic acid recycled powder, which required some new cobalt to be added in order to bring the cobalt depleted stoichiometry back to 6wt%, contained some visible (discrete) cobalt grains, in the same way as the new powders, but displayed very angular WC grains akin to the zinc recycled material. The acetic acid material contained very coarse particles as well as very fine particles in the same slurry, as evidenced in Figure 4-34, compared to the other grades which were more homogeneous in their grain size distributions. The most homogeneous particle size distributions were found in the new powders. PRZ powders contained a wider distribution than the new powders, but not as wide as the acetic acid material. Figure 4-35 shows the overall grain size distribution curves of the various slurries. Rather than the simple D10, D50, D90 and Mv values of Table 9 (page 112), the overall graphical distribution can highlight differences that are not necessarily seen in numerical data. For example, AC-lab most notably possessed the widest overall particle size distribution, with very fine grains and some very coarse grains, in agreement with the SEM images of Figure 4-34. The PRZ slurries had coarser particles than the new powders except for NP-prod-remill, which was intentionally milled to a coarse size, to test the effects of coarse particle size on a new powder slurry and compare to its PRZ counterparts.

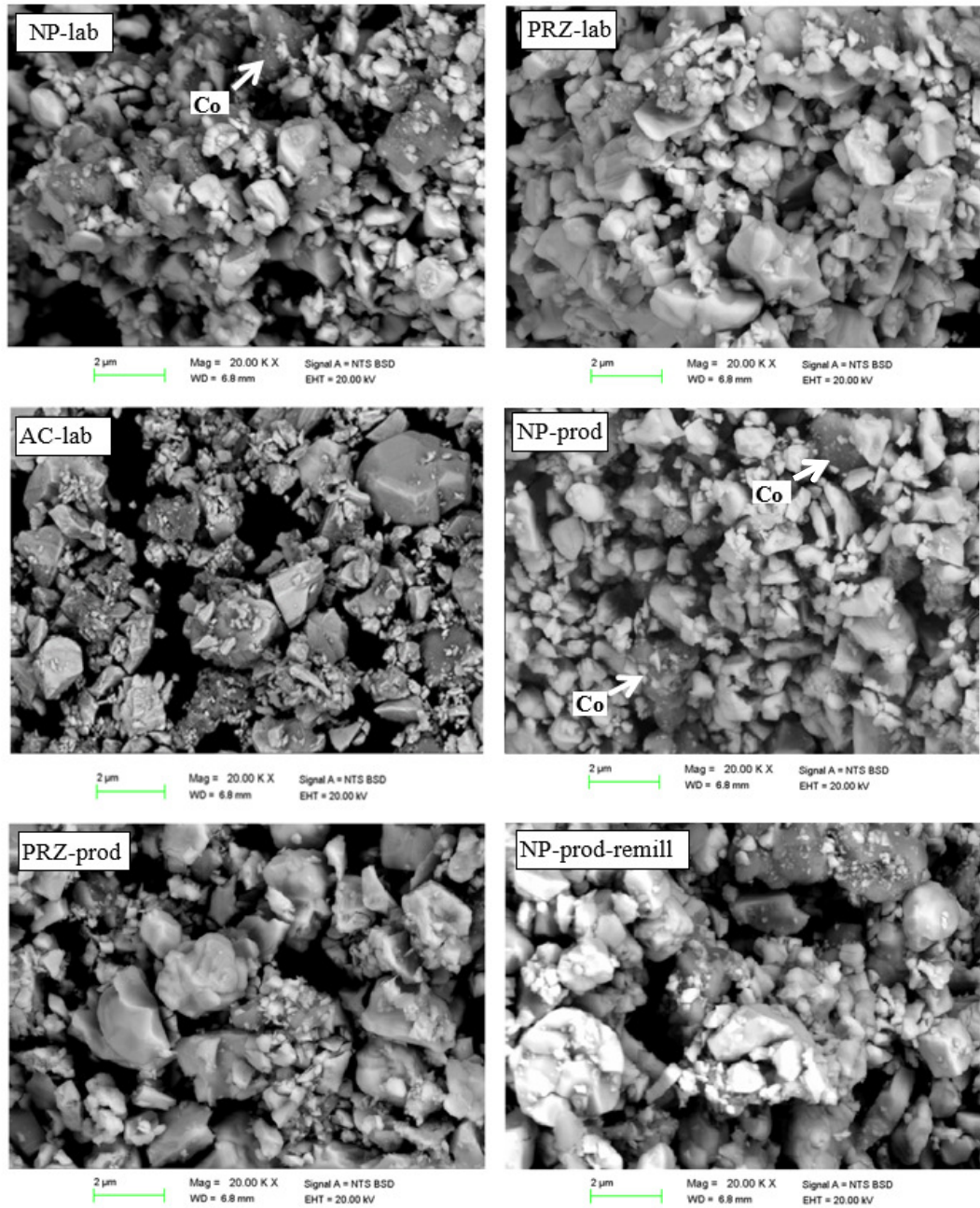


Figure 4-34 SEM micrographs at 20000X magnification, showing the microstructure of the slurries spray dried in this work. The dark phase corresponds to cobalt binder, with the lighter, more angular grains depicting WC.

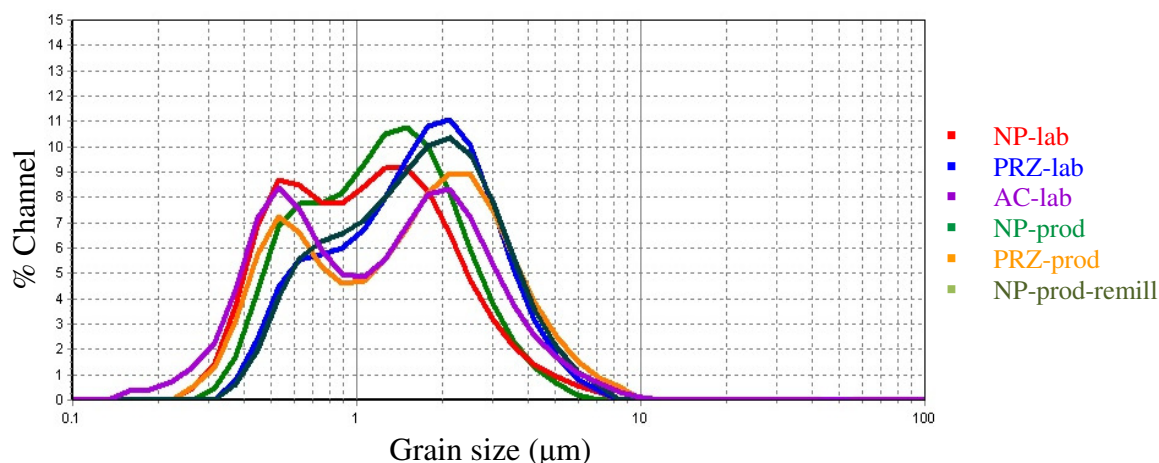


Figure 4-35 Overall grain size distribution curves of the various powders studied using slurry rheology.

4.6.3.3 Settling tests

Settling test results of all of the powders at a high solids loading of 11.89wt% ethanol are shown in Figure 4-36, which reflects apparent viscosity as a function of settling time. The legend shows the ranking order of the powders, from highest to lowest final apparent viscosity, which also reflects the order of increasing particle size. The figure shows clearly that the viscosity decreased with an increase in particle size. When comparing only NP to recycled powders, the NP-prod and NP-lab powders experienced higher and greater changes in viscosity with time compared to PRZ-prod, PRZ-lab and AC-lab powders, where the viscosity changes were minimal over the 1800s of testing time. The recycled PRZ powder graphs show an almost horizontal line of viscosity as a function of time. As time progressed, the laboratory milled NP-lab powder had a higher viscosity than the production milled NP-prod powder.

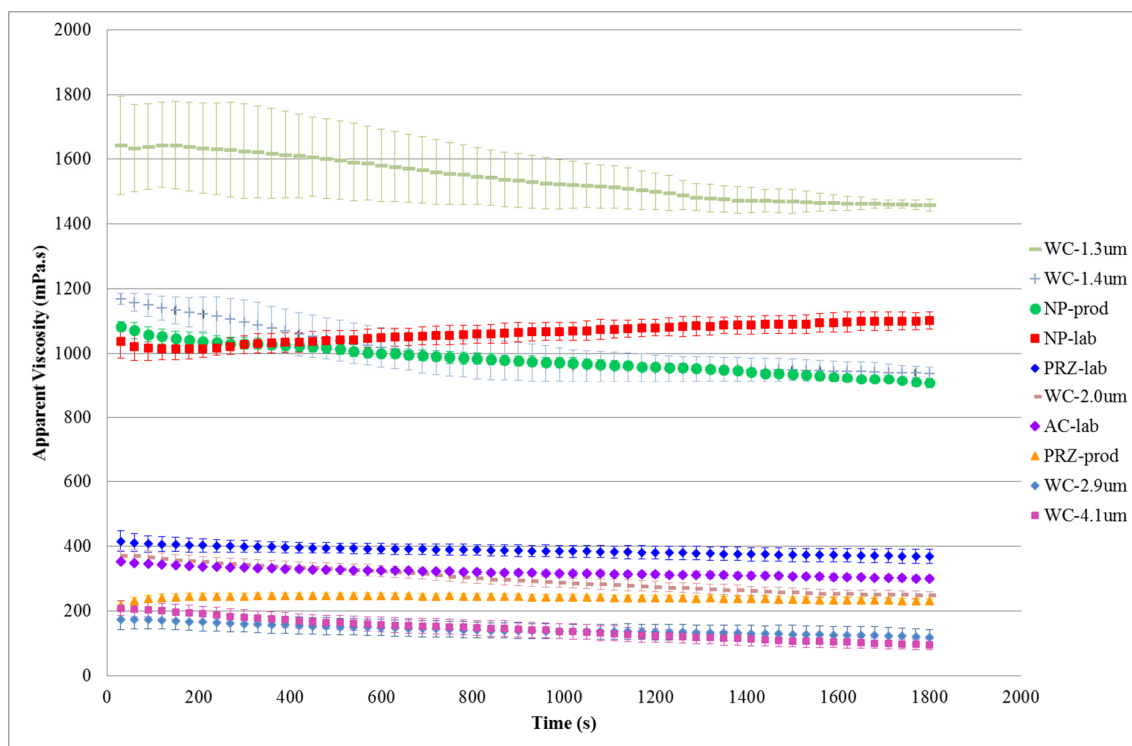


Figure 4-36 Settling rate comparison between the various powders measured at 11.89wt% ethanol (a high solids loading condition) at a shear rate of $65s^{-1}$ for 30 minutes.

4.6.4 Slurry rheology of bulk (spray dried) slurries

The rheology of each of the spray dried slurries is reported here ‘as-sprayed’, i.e. prepared with the corresponding alcohol content used for spray drying.

4.6.4.1 Rheology at low solids loading

The NP-lab, PRZ-lab and AC-lab powders were spray dried at 16.67wt% alcohol. The shear stress as a function of shear rate for these slurries is shown in Figure 4-37. The production milled powders are also shown in the same figures, but are discussed in the following section (moderate solids loading conditions).

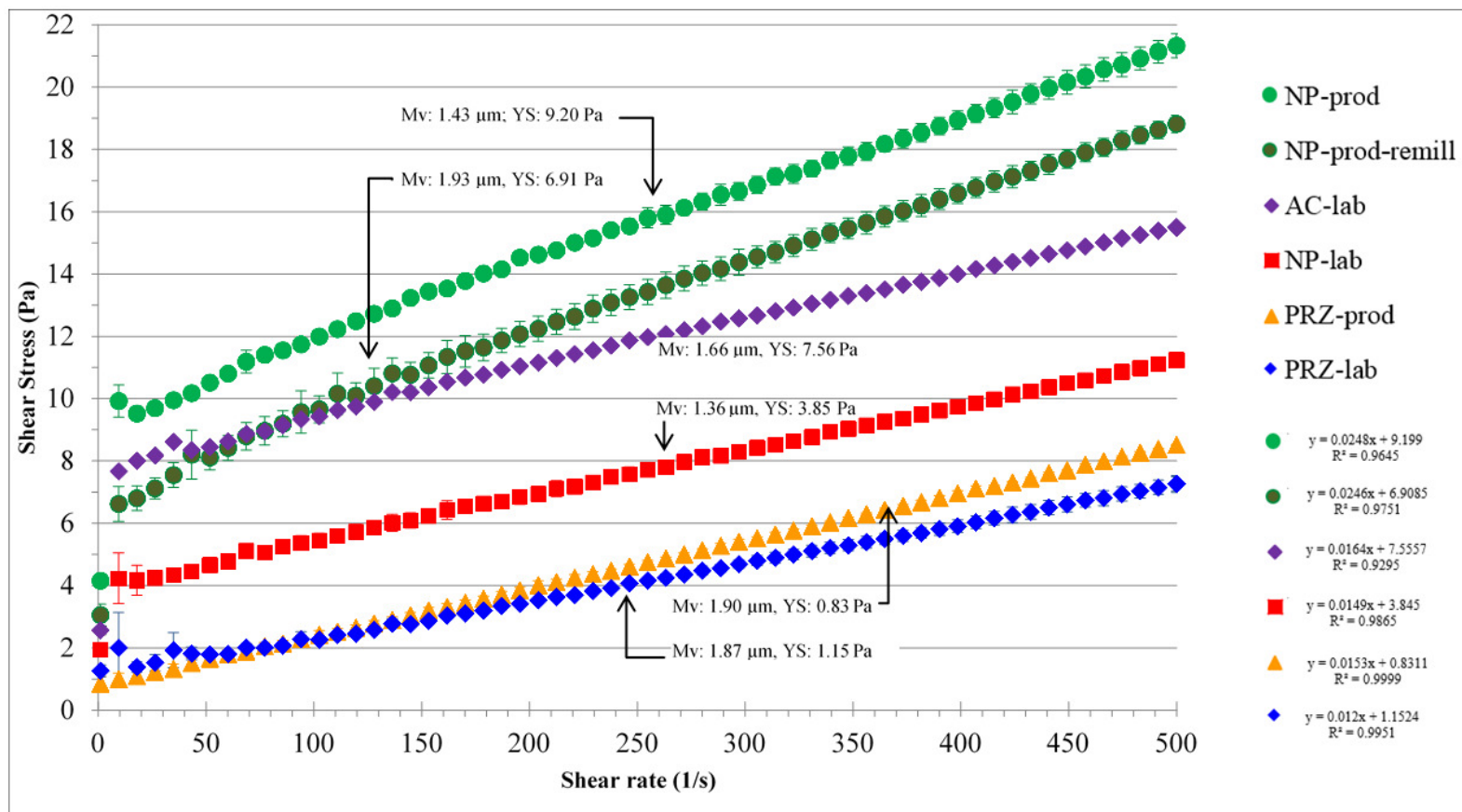


Figure 4-37 Shear stress against shear rate comparison measured at 16.67wt% ethanol for the laboratory milled powders and at 13.65wt% ethanol for the production milled powders. Mean volume grain size (Mv) and calculated yield stress (YS) are as indicated.

The decelerating curves, which overlap the accelerating curves, have been omitted for ease of comparison. NP-lab has a higher shear stress and smaller Mv than PRZ-lab. The yield stress of NP-lab was calculated to be 3.85Pa, while PRZ-lab had a low yield stress of 1.15Pa. The yield stress of AC-lab was 7.56Pa, despite its coarse Mv particle size, AC possessed a higher than expected viscosity and yield stress.

The results of the settling tests of NP-lab and PRZ-lab are shown in Figure 4-38. A linear plot has been fitted to each curve with the equation shown on the graph (Figure 4-38). The gradient of the straight line indicates that NP-lab had a higher settling rate than PRZ-lab, with larger changes in viscosity occurring over the same time period. AC-lab had the highest viscosity of the laboratory milled powders, but experienced a similar settling rate.

4.6.4.2 Rheology at moderate solids loading

The NP-prod, PRZ-prod and NP-prod-remill powders were spray dried at 13.65wt% ethanol. The shear stress as a function of shear rate is shown in Figure 4-37, with the Mv and yield stress for each slurry. Similar to the laboratory milled and spray dried powders (16.67wt% ethanol), the production milled and spray dried NP-prod had a higher shear stress against shear rate than the PRZ-prod. NP-prod-remill had a lower shear stress against shear rate and a lower yield stress than NP-prod, but had a coarser grain size; 1.93 μ m compared to 1.43 μ m. PRZ-prod possessed a low yield stress of 0.83Pa.

The results of the settling tests for NP-prod, PRZ-prod and NP-prod-remill are shown in Figure 4-38. The settling rates, indicated by the gradient of the linear lines fitted to the data, of NP-prod and NP-prod-remill were similar, at -0.016 and -0.017 respectively. The most stable slurry was PRZ-prod with a gradient of -0.0038.

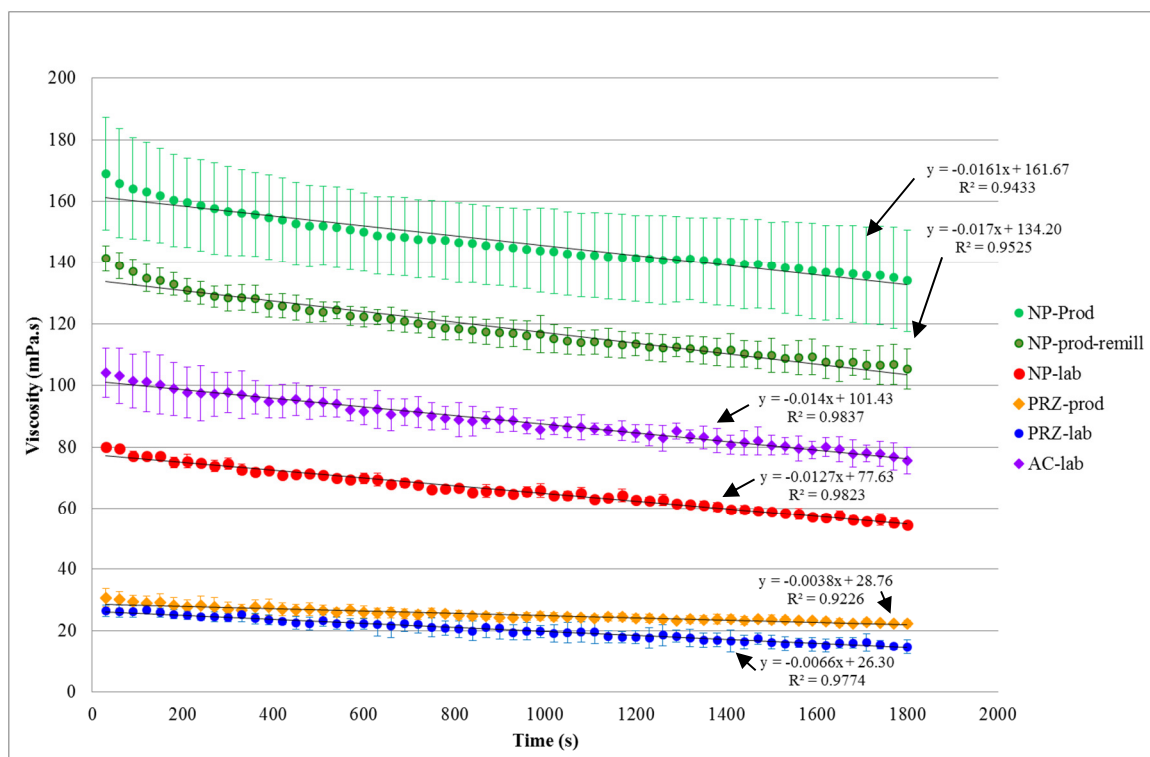


Figure 4-38 Settling rate comparison between experimentally (lab) milled WC-6% Co powders, measured at 16.67wt% ethanol (i.e. the conditions used for spray drying these powders); similarly, the settling rate curves for NP-prod, NP-prod-remill and PRZ-prod as measured at 13.65wt% ethanol are shown, as well the fitted linear equations for each curve.

4.7 Powder rheology

The powder rheology results are presented in this section. The chapter begins with dynamic flow analysis followed by shear results, compressibility, friction behaviour and finally the powders' response to air flow is presented.

4.7.1 Dynamic analysis

Repeatability and variable flow rate graphs are shown in Figure 4-39 (p 127), where the flow energy (mJ) is plotted against the test numbers.

Tests 1 to 7 correspond to a tip speed of 100mm/s of the rheometer blade, and test number 8 to 10 decreased in tip speed to test the powders under a changing flow rate from 100mm/s down to 10mm/s. The highest flow energies, under constant flow and variable flow conditions, belonged to the humidified powders. The NP-lab and PRZ-lab humidified powders increased their flow energy by similar amounts i.e. between 700 to 1000mJ per test in the constant flow rate regime, compared to the original NP-lab and PRZ-lab powders which possessed more stable flow energies of ~5500mJ and ~5200mJ respectively (test number 1-7). Under variable flow conditions (tests 8-11), the humidified powders underwent a dramatic increase in flow energy as the tip speed decreased, with flow energies at 10mm/s of 7500mJ and 7000mJ for NP-lab humidified and PRZ-lab humidified powders respectively, compared to approximately 5800 and 5600mJ for the same powders in the dry state.

In the dry state, the powders fell into 3 'energy bands' based upon their particle size distribution. These bands (energy ranges) have been indicated on Figure 4-39 and are numbered 1 to 3. Band 1 ranged from 3400mJ to 3800mJ in which the coarsest (150-180µm) powders possessed overlapping flow energy curves that were almost indistinguishable from each other. Band 2, ranging from 3900mJ to

4300mJ, encompassed the energy curves for 90-125 μ m powders, but with the flow energy curves more widely separated (less overlap) than the 150-180 μ m powders (band 1). Band 3, ranging from 4600mJ to 5600mJ (not including the humidified powders), covers the energy range for the 45-63 μ m powders, with each powder flow curve clearly distinguishable.

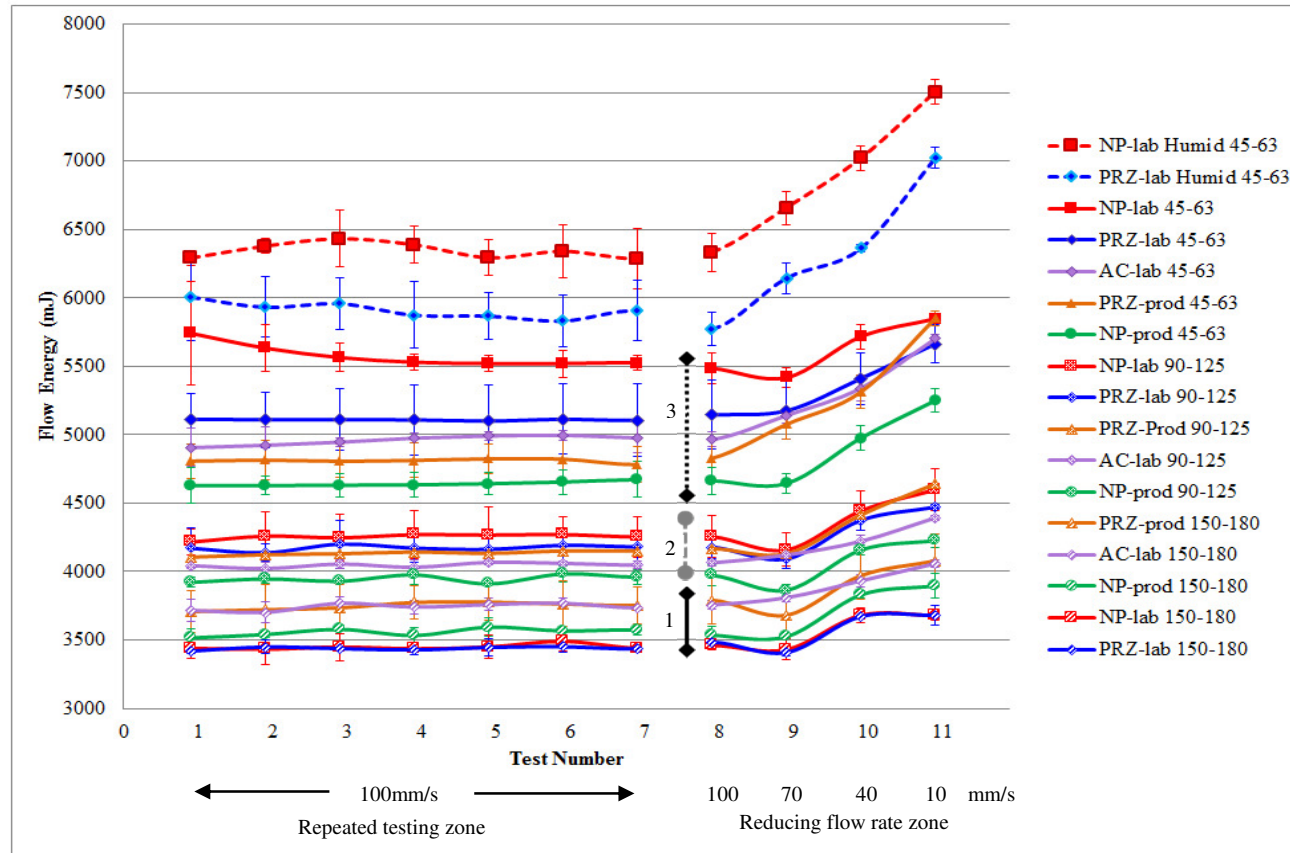


Figure 4-39 Dynamic test results (repeatability and variable flow rate) for the various dry powder screen fractions (solid lines) and humidified NP-lab and PRZ-lab 45-63 μ m powders (dotted lines), with tests 1-7 showing the repeated testing zone results tests 8-11 displaying the reducing flow rate zone results. The legend rank order corresponds to that of the powder results.

NP-prod fell at the bottom energy bands 2 and 3, having the lowest flow energy, again with a low flow energy (almost overlapping with NP-lab, PRZ-lab and AC-lab) in band 1. In band 3, the highest average flow energy (under constant flow) corresponded to NP-lab (5525mJ), followed by PRZ-lab (5106mJ), AC-lab (4960mJ) then PRZ-prod (4782mJ) and NP-Prod (4672mJ). The same trend occurred in band 2, with NP-lab (4253mJ), PRZ-lab (4180mJ), PRZ-prod (4151mJ) and then AC-lab (4050mJ) and NP-prod (3959mJ). In band 1, the average flow energies from most to least were: PRZ-prod (3754mJ), AC-lab (3744mJ), NP-prod (3574mJ), NP-lab (3441mJ) and PRZ-lab (3438mJ) but with experimental errors and smaller energy differences (overlapping graphs) between powders especially apparent on Figure 4-39.

Under the variable flow rate testing regime (tests 8-11), the powders experienced a flow energy change, indicated by the flow rate index (FRI) factor (the factor by which the flow energy changed with an order of magnitude change in flow rate i.e. this is the ratio of the flow energies of test 8 and test 11). For band 1 and 2 the FRI of the dry powders was between 1.06 to 1.11 ± 0.02 for all of the powders, indicating very similar and consistent flow energy changes as the tip speed decreased. For band 3 (the finest powders) the FRI ranged between 1.07 to 1.15 ± 0.03 for NP-prod, PRZ-lab, AC-lab and NP-lab, with only PRZ-prod having a distinguishably higher FRI than the others, of 1.21 , which can also be seen by the steeper gradient of this powder's curve in the reducing flow rate zone on Figure 4-39. For the humidified powders, the FRI was 1.18 ± 0.01 and 1.22 ± 0.04 for NP-lab and PRZ-lab humidified powders respectively.

4.7.2 Shear results

The shear curves for the various powders are shown in Figure 4-40, in which shear stress (kPa) has been plotted against applied normal stress (kPa). The differences between the powders were less clear than the dynamic analysis results, but the powders still ranked primarily according to their particle size. PRZ-prod (45-63 μ m) had the highest shear stress at each applied normal stress, with PRZ-lab humid, AC-lab and NP-lab humid following. The remaining 45-63 μ m powders had the next highest shear response, followed by the coarser particles, most of the 90-125 μ m powders required more stress to shear them, compared to the 150-180 μ m fractions. Many of the data points overlapped, with large enough uncertainty to occlude any noticeable trend based purely upon powder composition or recycling history. The shear tests reported values for an angle of internal friction ranging between 21° and 26° for all of the powders with large errors of up to $\pm 1^\circ$ in some cases, making it difficult to distinguish trends, nevertheless this data has been shown in Table 9 (p 112). The humidified and finest powder fractions had a tendency for internal friction angles of 2 - 3° higher than the coarser powders.

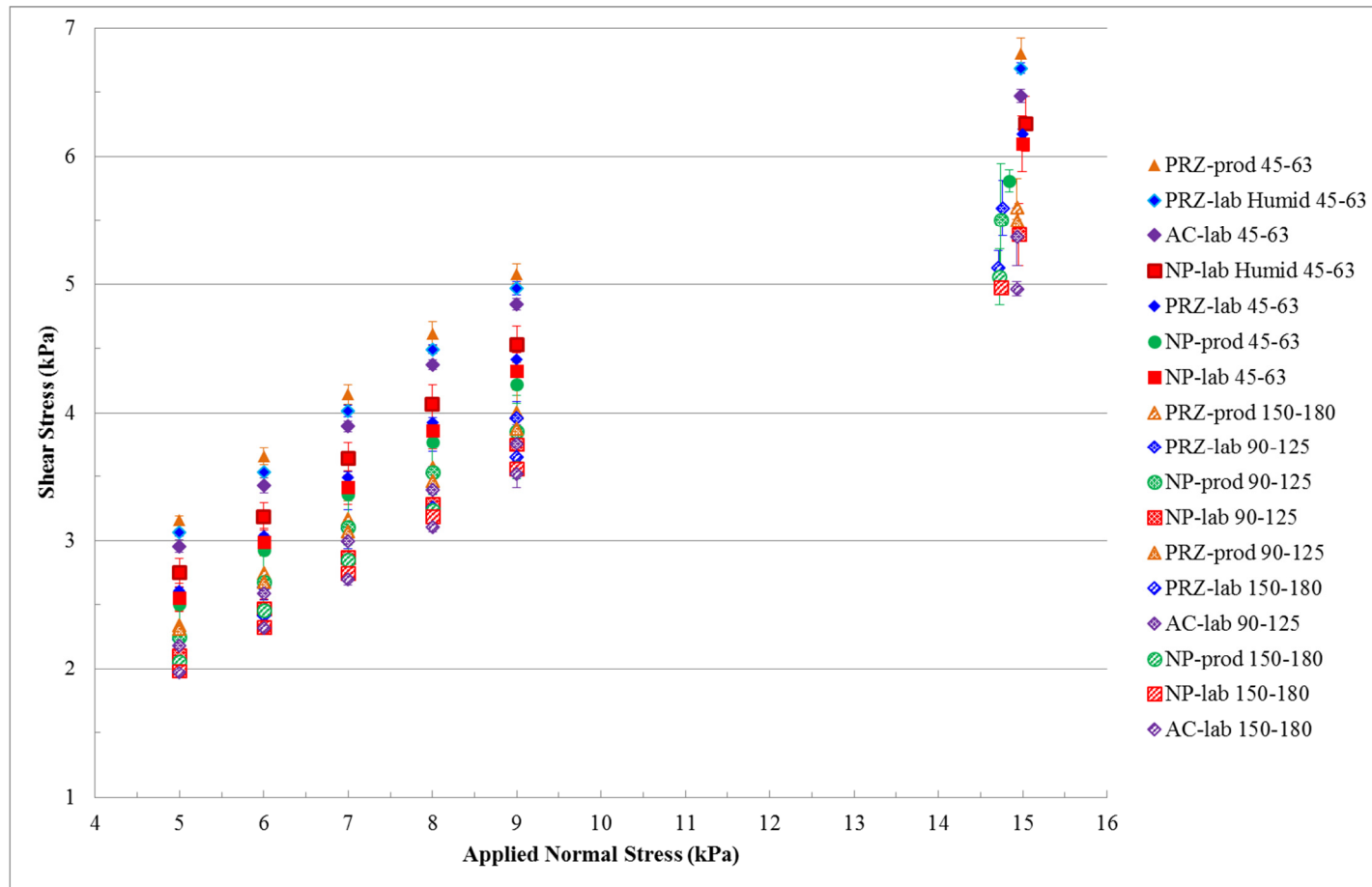


Figure 4-40 Shear test results (shear stress vs. applied normal stress) for the various dry and humidified powder screen fractions showing a great deal of overlap, but with finer powders towards the top of the curves and coarser powders lower down.

4.7.3 Powder compressibility

The compressibility curve of each powder from 1-15kPa applied normal stress is shown in Figure 4-41. The highest percentage compressibility belonged to humidified PRZ-lab 45-63 μ m powder, followed by overlapping compressibility curves of PRZ-prod, NP-lab humid and AC-lab 45-63 μ m powders. The remaining 45-63 μ m powders all overlapped with each other, followed thereafter by the coarser screen fractions of the other powders, with no clear trend based upon size or composition. The finest (and humidified) particles clearly ranked highest in terms of compressibility. PRZ-lab humid experienced ~1.7% more compressibility at 15kPa applied normal stress compared to its dry powder state, similarly NP-lab humid compressed by ~1% more than its dry counterpart.

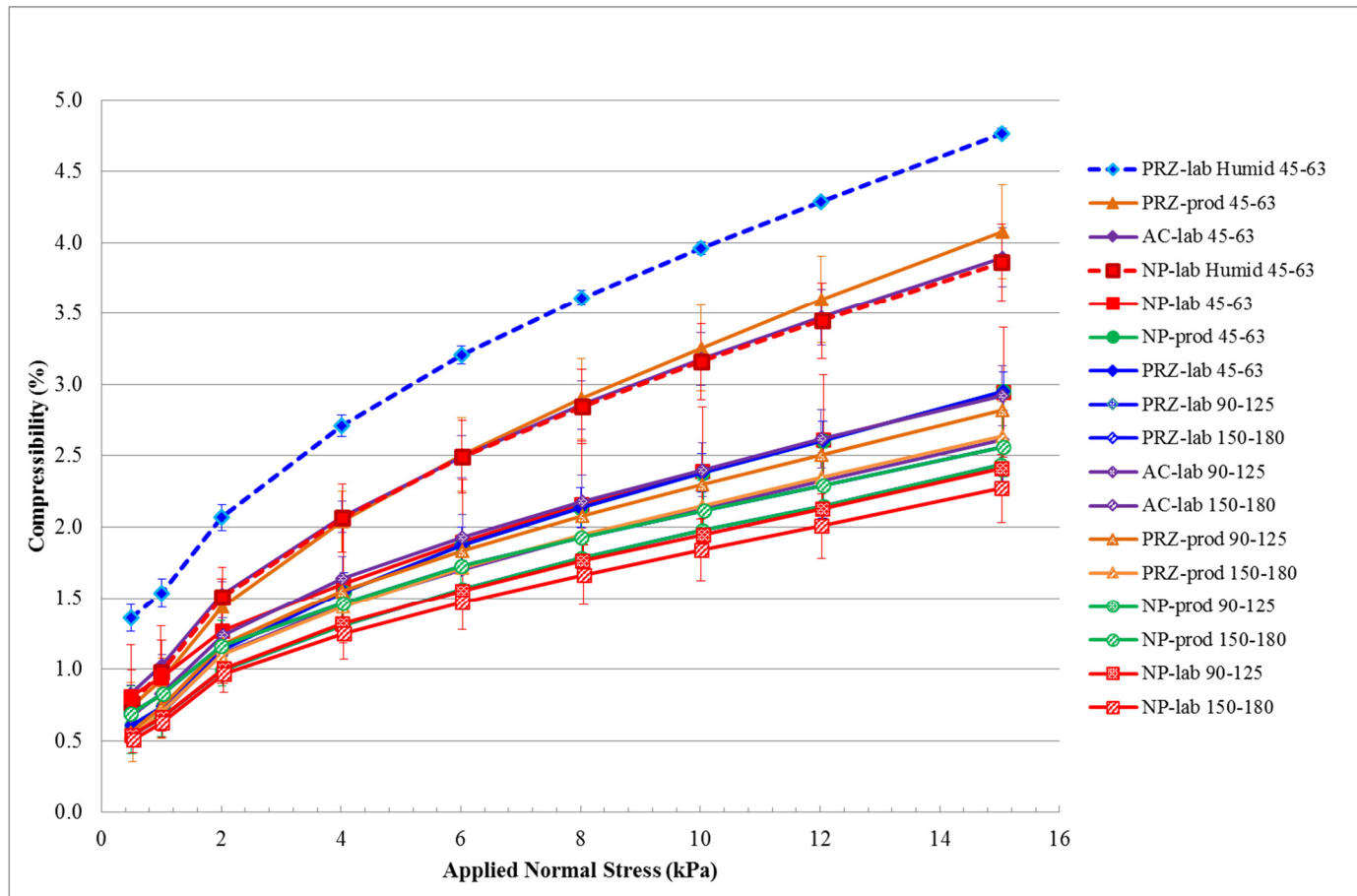


Figure 4-41 Compressibility curves of the various dry and humidified powders. The legend rank order corresponds to that of the powder results.

4.7.4 Wall friction

Wall friction angles are shown in Table 11, and have been ranked from highest to lowest to highlight any trends. The 45-63 μ m dry powders all had wall friction angles of between 16° to just above 18° (in the case of NP-lab, which has the overall highest wall friction angle of 18.26°, followed by PRZ-lab at 17.65°). The errors of the measurements were small enough to be able to distinguish the fine powders from their coarser counterparts. The coarser powders ranged between 14° and 15° for the 150-180 μ m powders, and around 15° to just over 16° for the 90-125 μ m screen fractions. NP-lab experienced a drop of wall friction angle in the humidified state by 2.8°, and PRZ-lab by 1.24°.

Table 11: Wall friction and internal friction angles from the wall friction test and shear test of the FT4 powder rheometer, and associated errors.

Powder	Wall friction angle (°)	Angle of internal friction (°)
NP Lab 45-63	18.26 $\pm$ 0.09	23.82 $\pm$ 0.70
PRZ Lab 45-63	17.65 $\pm$ 0.50	24.25 $\pm$ 0.57
AC-lab 45-63	16.47 $\pm$ 0.15	25.20 $\pm$ 0.73
PRZ Lab 45-63 Humid	16.41 $\pm$ 0.30	25.51 $\pm$ 0.26
NP Prod 45-63	16.19 $\pm$ 0.10	23.18 $\pm$ 0.85
NP Lab 90-125	16.05 $\pm$ 0.43	22.33 $\pm$ 0.62
PRZ Prod 45-63	15.97 $\pm$ 0.41	25.60 $\pm$ 0.48
PRZ Lab 90-125	15.76 $\pm$ 0.19	23.51 $\pm$ 1.00
NP Lab 45-63 Humid	15.46 $\pm$ 0.16	23.95 $\pm$ 0.28
PRZ Prod 90-125	15.21 $\pm$ 0.29	21.36 $\pm$ 0.42
NP Prod 90-125	15.18 $\pm$ 0.32	22.17 $\pm$ 0.75
PRZ Prod 150-180	14.93 $\pm$ 0.31	22.47 $\pm$ 0.93
AC-lab 90-125	14.80 $\pm$ 0.10	21.67 $\pm$ 0.76
AC-lab 150-180	14.53 $\pm$ 0.45	21.27 $\pm$ 0.71
NP Prod 150-180	14.38 $\pm$ 0.49	20.77 $\pm$ 0.20
PRZ Lab 150-180	14.23 $\pm$ 0.07	22.09 $\pm$ 0.02
NP Lab 150-180	14.15 $\pm$ 0.06	21.92 $\pm$ 0.38

4.7.5 Aeration, de-aeration and permeability

Testing revealed three distinct powder responses to fluidization and aeration experiments based predominantly on powder particle size shown in Figure 4-42. The finest fraction of all of the powders whether humidified or not, fluidized (requiring close to zero energy to flow hence behaving like a fluid) at 15mm/s air velocity, with overlapping flow energy against air velocity profiles. The medium fraction (90-125 μ m) of all powders fluidized around 30mm/s and the coarsest fraction (90-125 μ m) did not fluidize even at the maximum air velocity allowed by the FT4 powder rheometer system. The powders behaved similarly in their respective fluidization bands, with no clear difference based upon composition (new vs recycled powders) because both PRZ-lab and NP-lab (the 100% new and 100% recycled) curves overlapped in many cases. Humidity also had no effect on fluidization in this case. NP-prod and PRZ-prod, however, required more energy to flow than the other powders for most of their data points in each size range.

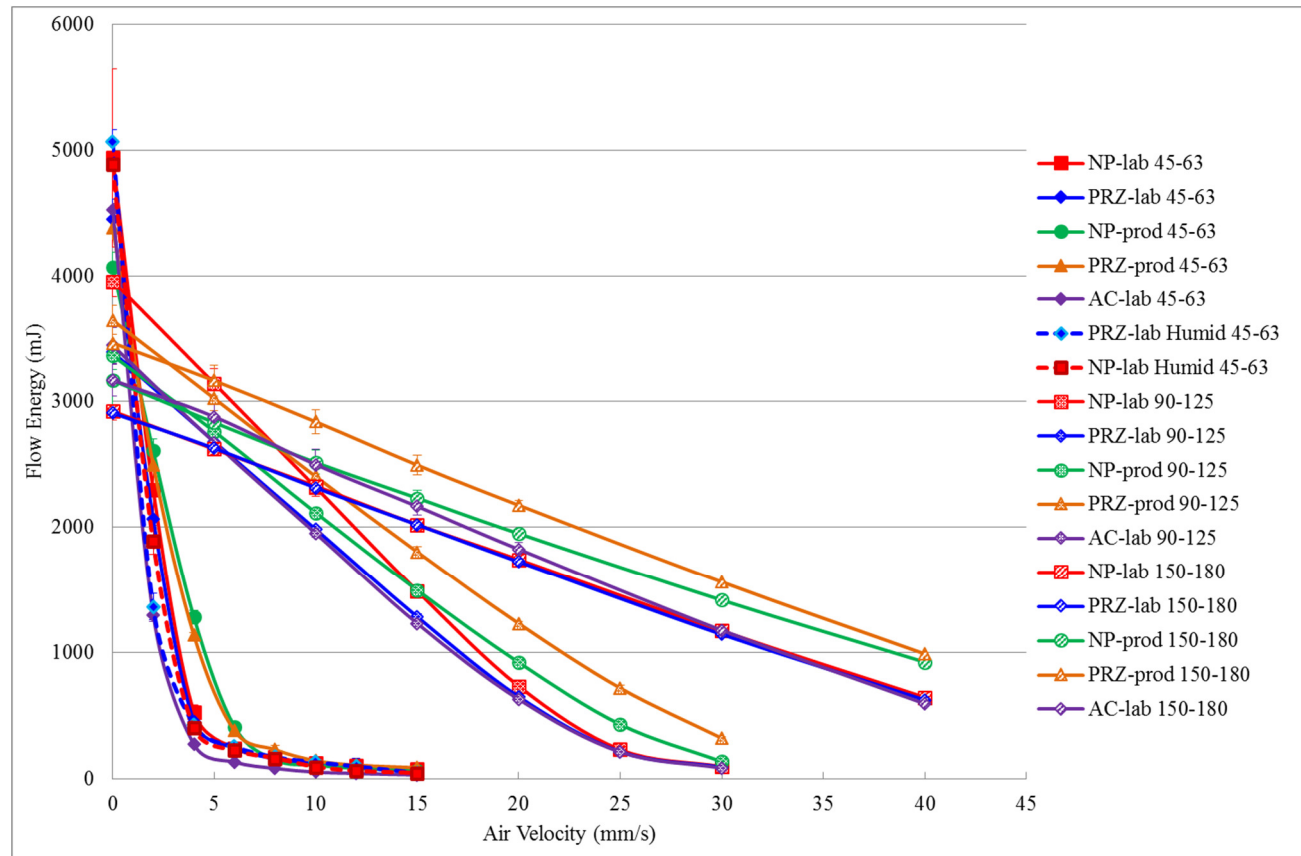


Figure 4-42 Aeration testing and fluidization results for the various powders, showing 3 distinct zones based upon particle size. The 45-63µm powders all completely fluidized by 15mm/s air speed, the 90-125µm powders fluidized between 30 and 35mm/s, while the 150-180µm screen fractions did not fluidize at all at the maximum air speed of 40mm/s.

The results for the de-aeration behaviour of each powder are shown in Figure 4-43. The humidified powders showed the greatest tendency to retain air, shown by the steep flow energy change (the gradient) between zero de-aeration cycles and 1 cycle on the graphs in Figure 4-43. The retained air reduced the flow energy of NP-lab humid by ~1200mJ, and PRZ-lab humid by ~800mJ. After one de-aeration cycle, both humidified 45-63 μ m powders released their air and stabilized, maintaining more consistent flow energies, but higher than their dry counterparts as was the case with previous flow energy results. The remaining dry 45-63 μ m screen fractions possessed the next highest flow energies with less air retention, only changing flow energies by ~400mJ for PRZ-lab and NP-lab 45-63 μ m powders. The NP-prod and PRZ-prod 45-63 μ m powder flow energy changed by approximately 100mJ, on average, in response to de-aeration testing. The AC-lab 45-63 μ m fraction changed by approximately 700mJ. The 90-125 μ m and 150-180 μ m screen fraction results for all of the powders were similar, showing little or no change with de-aeration, however the 90-125 μ m screen fraction powders consistently possessed higher flow energies than the coarser fractions (as before) with many overlapping data points between powder batches in each size range.

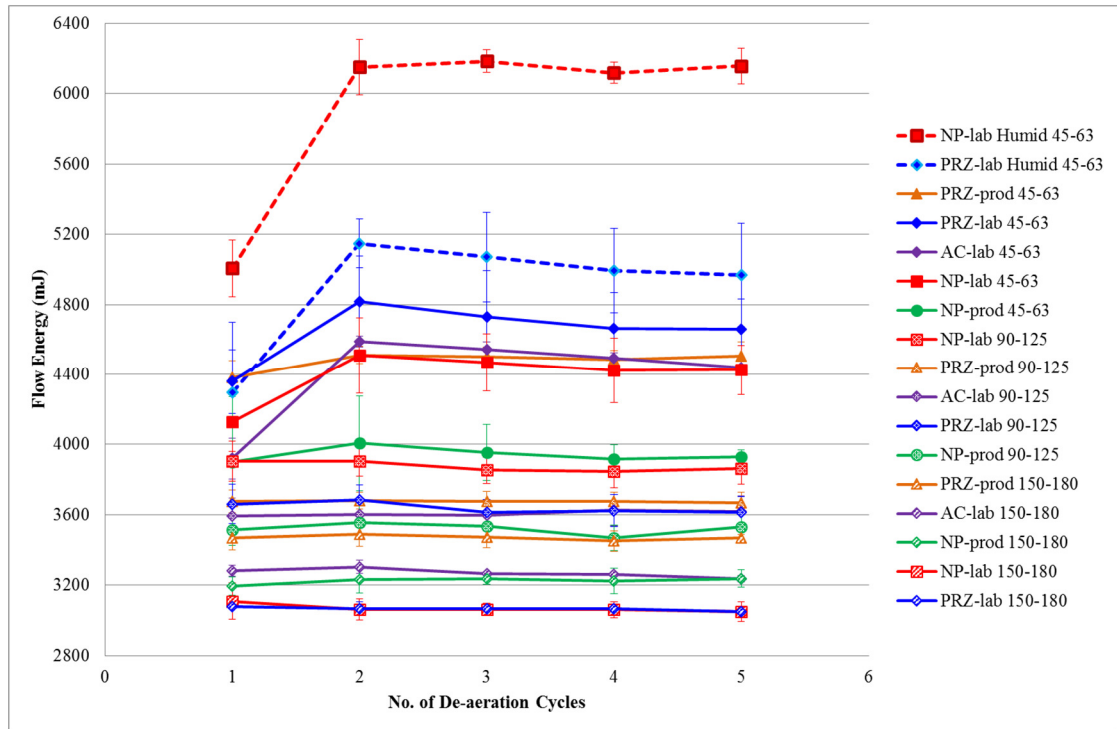


Figure 4-43 De-aeration tests in which flow energy (mJ) from 0 to 4 de-aeration test cycles was measured.

Powder permeability was measured and plotted on Figure 4-44 as the pressure drop across the powder bed, against the applied normal stress from 1 to 15kPa. Air pressure dropped the most across the humidified powder beds and AC-lab, with PRZ-lab humid dropping by 21 mbar (millibars) at 15kPa normal stress and 13 mbar in the case of NP-lab humid. The NP-lab humid powder experienced an increased pressure drop of 2 mbar compared to its dry counterpart, and PRZ-lab humid increased by an 8 mbar pressure drop compared to dry NP-lab powder. PRZ-lab and NP-lab 45-63 μ m screen fractions experienced similar pressure drops across the applied normal stress range, of 10-11 and 11-12 mbar respectively. AC-lab was less permeable, measuring a pressure drop of 13-14 mbar. PRZ-prod 45-63 μ m experienced a pressure drop of around 9 mbar across the stress range, while NP-prod 45-63 μ m was the least affected powder in its size range, undergoing a pressure drop of only 7-8 mbar. Partial overlap occurred in the case of 90-125 μ m powder results, and a complete overlap for the 150-180 μ m powder results.

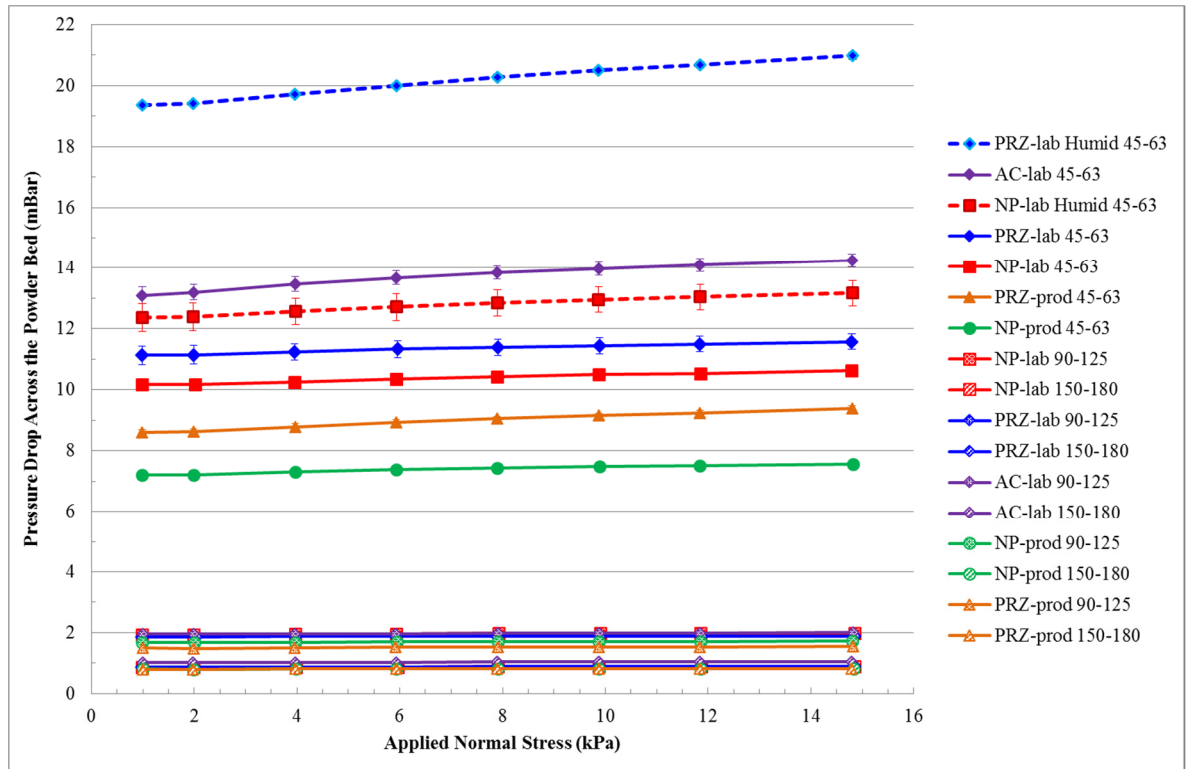


Figure 4-44 Permeability of the various powders showing the pressure drop across each powder bed plotted against the applied normal stress. Only the 45-63 μ m powders (but especially the humidified powders) displayed notable differences in permeability.

4.8 Sintered material characterization

The results of the various techniques used to characterize the sintered materials are presented in this section.

4.8.1 Micro-PIXE of sintered materials

Figure 4-45 and 4-46 show SEM images of the sintered microstructures with the corresponding W_L, Co and Fe micro-PIXE composition maps. The SEM images

associated with the micro-PIXE maps have been provided to allow for an easy comparison of the microstructure with the micro-PIXE results. The light phase on the SEM micrographs is WC with the dark (or black) regions showing the Co binder phase. Please note that the high intensity of some of the W_L maps can make comparison difficult, hence the Co map is most useful. If the intensity (which is a built-in automatically scaled function in the mapping software that is not alterable) was not the same between the grades, then each map's individual scale bar has been shown adjacent to the map.

Distinct differences in the homogeneity of the microstructures are evident from Figure 4-45 and 4-46. The best distribution of Co was found in grade PRZ-prod followed by PRZ-lab with the worst distribution found in the new powders. AC-lab also showed inferior homogeneity of cobalt compared to the PRZ grades, possessing a larger grain size than the other materials when comparing the SEM micrographs. From these results it is apparent that the microstructural inhomogeneity which was evident in the new powders persisted in the sintered material despite the use of sinter-HIP densification. The Fe levels in the sintered materials followed the same trend found in the powders where the highest Fe levels were detected in grade PRZ-lab. The interesting observation of the Fe mapping in the sintered materials was that for each grade, the highest Fe levels were found in the Co binder regions. This is seen by comparing the Fe and Co maps for each grade. Grade NP-lab showed Fe levels of approximately 0.4 to 0.8wt% while grade PRZ-lab had Fe levels from 0.4wt% to in excess of 1 to 1.5wt%, and AC-lab ranged from 0.1 to a maximum of 0.6wt%. Grade PRZ-prod displayed Fe concentrations typically below 0.2wt%. NP-prod possessed similar iron concentrations to AC-lab, ranging from 0.1 to 0.8wt% with both possessing an average of approximately 0.4wt% Fe. Circled regions numbered 1 to 4 on Figure 4-45 and 4-46 highlight notable inhomogeneities in the materials and are explained further in the discussion chapter.

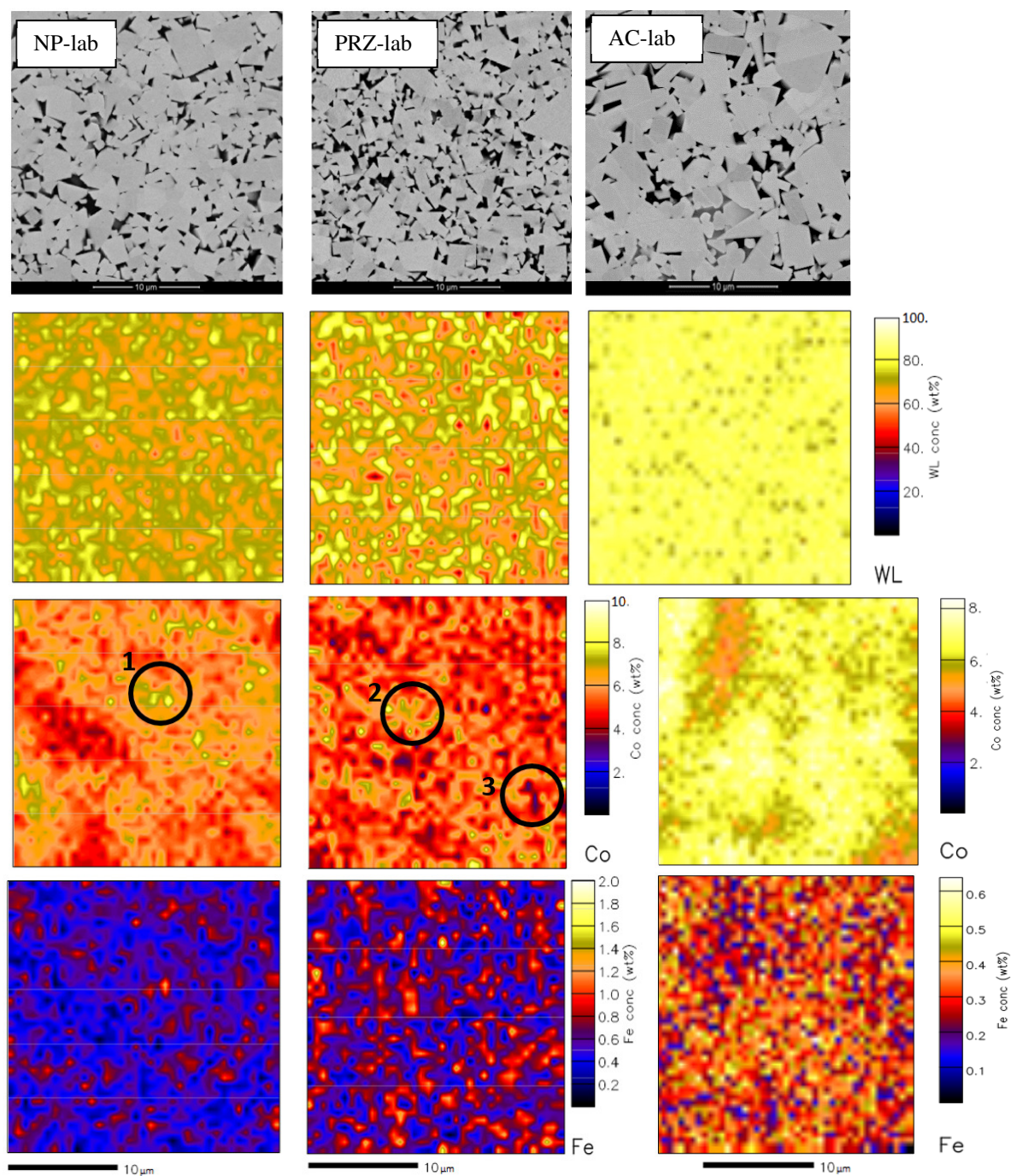


Figure 4-45 Sintered and polished NP-lab, PRZ-lab and AC-lab materials. Top: SEM micrographs taken at 10000x magnification in backscatter mode, 2nd row: Tungsten 'L' (WL) micro-PIXE maps, 3rd row: Co maps, bottom row: Fe maps.

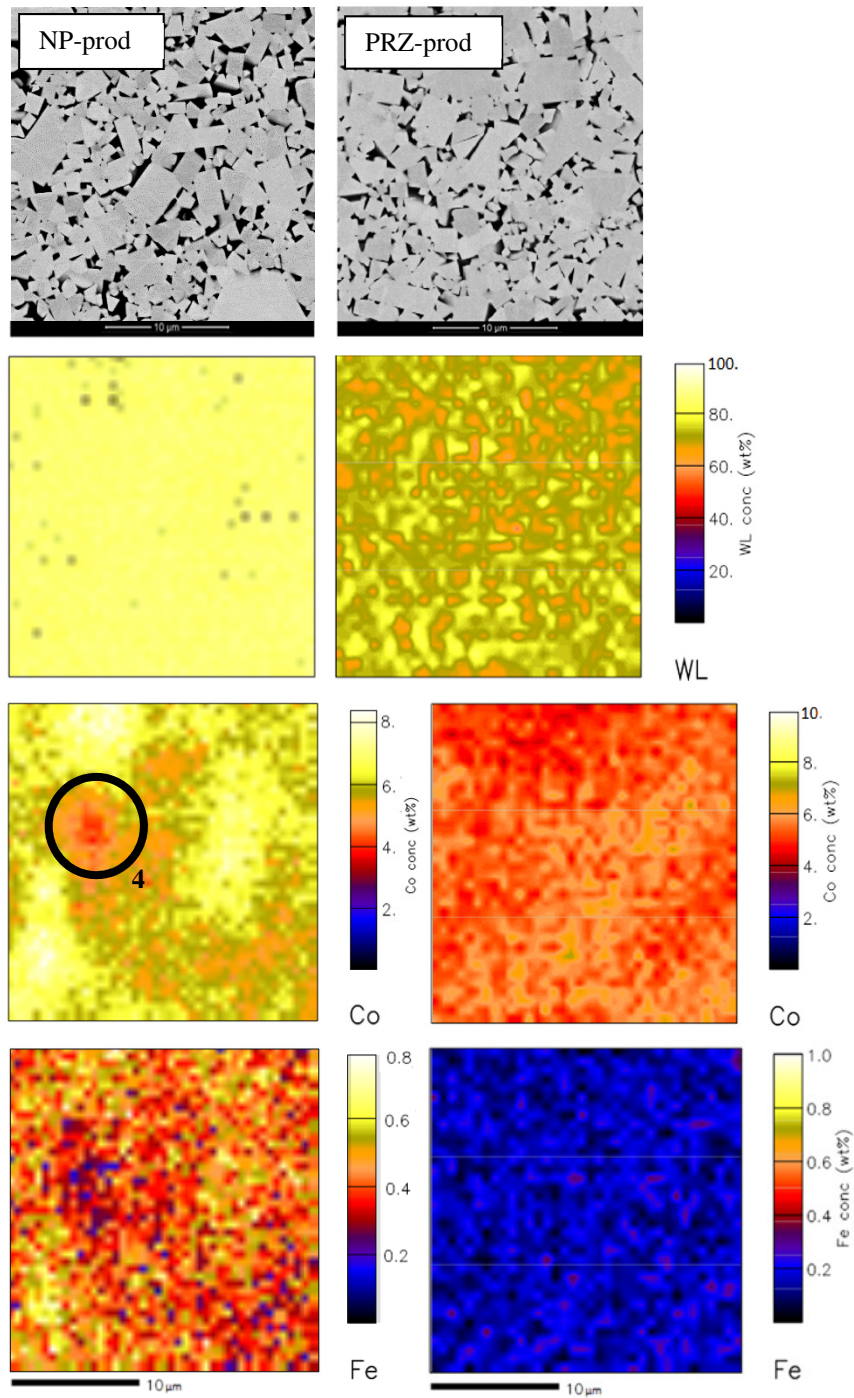


Figure 4-46 Sintered and polished NP-prod and PRZ-prod materials. Top: SEM micrographs taken at 10000x magnification in backscatter mode, 2nd row: Tungsten 'L' (WL) PIXE maps, 3rd row: Co maps, bottom row: Fe maps.

4.8.2 Scanning electron microscopy

High magnification backscattered SEM micrographs of the sintered microstructures of each grade are shown in Figure 4-47. EDS data for each grade is listed in Table 12. Traces of Fe were found in the binder regions of grades NP-lab, PRZ-lab, AC-lab and NP-prod. Isolated traces of Cu and Cr were detected in AC-lab and NP-prod respectively, but not in the other grades.

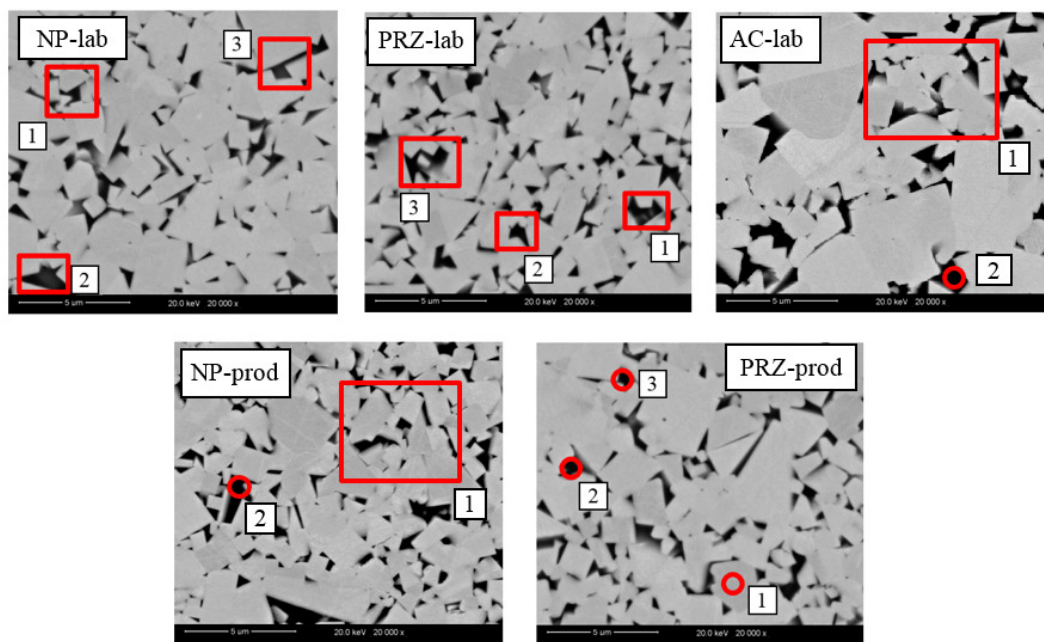


Figure 4-47 Backscattered SEM micrographs (20000X) of the sintered microstructures upon which EDS was performed. EDS scans of the numbered regions of each image correspond with the EDS data in Table 12. A rectangle indicates an area scan, a circle indicates a spot scan.

Table 12: Elemental composition (in wt% at 20keV) of the EDS scans of the numbered regions from Figure 4-47 for the various sintered microstructures.

Material / area number	% C	% Co	% W	%Fe	% Other elements detected
NP-lab 1	9.31	5.62	85.06	-	-
NP-lab 2	7.93	12.64	78.24	1.19	-
NP-lab 3	7.76	15.55	75.35	1.33	-
PRZ-lab 1	9.01	16.68	72.18	2.14	-
PRZ-lab 2	9.30	12.22	76.75	1.73	-
PRZ-lab 3	8.38	13.03	76.81	1.78	-
AC-lab 1	6.83	8.78	83.97	0.42	-
AC-lab 2	5.67	68.48	21.49	3.35	Cu: 0.84
NP-prod 1	7.57	7.21	84.67	0.55	-
NP- prod 2	5.93	45.48	45.01	3.13	Cr: 0.46
PRZ-prod 1	8.93	18.95	72.1	-	
PRZ-prod 2	10.81	6.21	82.97	-	
PRZ-prod 3	17.37	16.3	66.33	-	

In order to compare the grain size and microstructure of the sintered alloys, scanning electron micrographs were taken at 5000X magnification as shown in figure 4-48, and at 10000X magnification as shown in figure 4-49. Both NP-lab and NP-prod had a finer sintered grain size than the PRZ materials. Although the PRZ materials have some fine grains visible, a number of large grains are present in the micrographs. The largest overall grain size belonged to AC-lab, with some grains exceeding 10 μ m in size. The new powders did not show any signs of large, or isolated grains above 5 μ m in diameter.

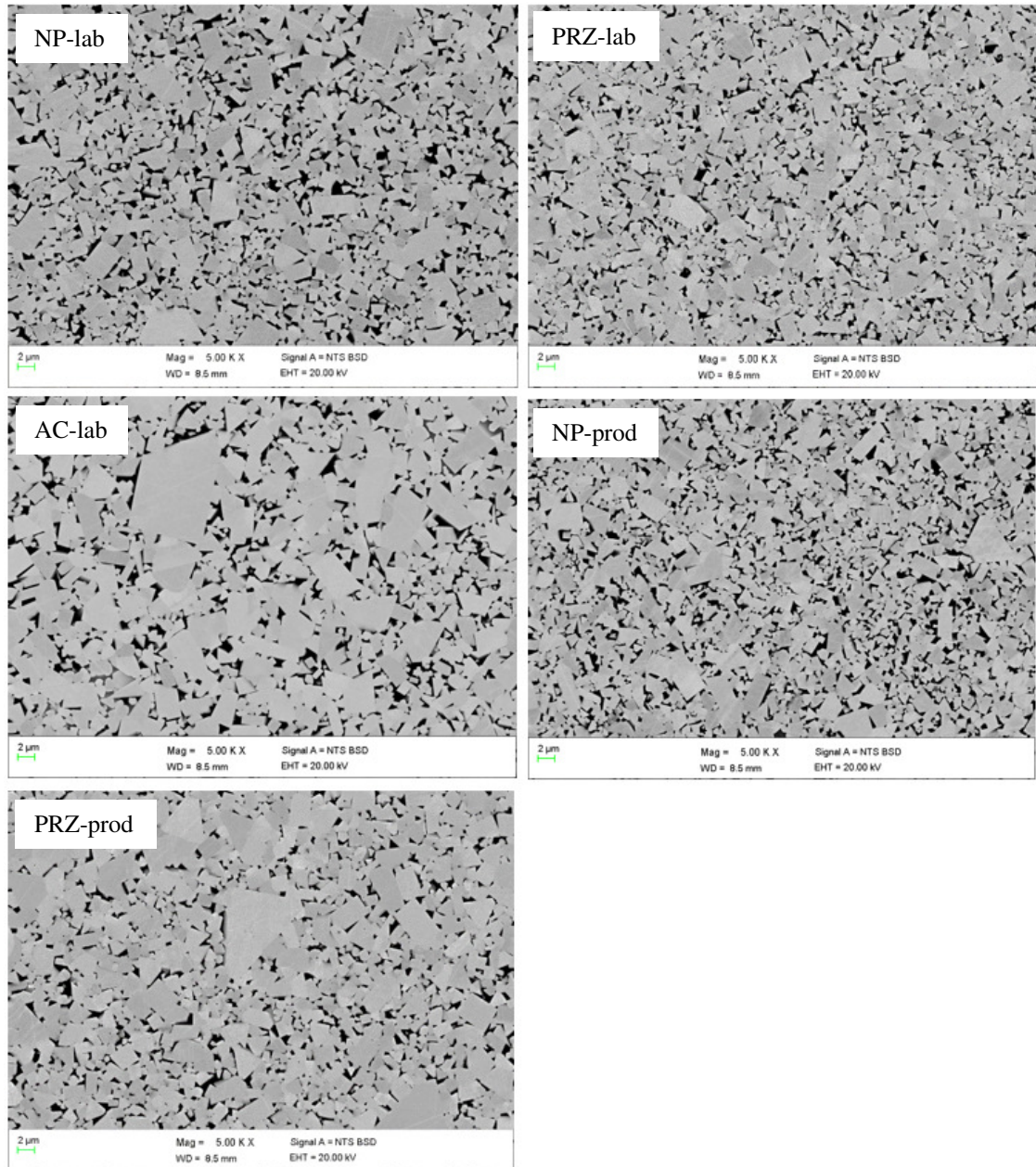


Figure 4-48 SEM micrographs of the sintered alloys at 5000X magnification in backscatter mode.

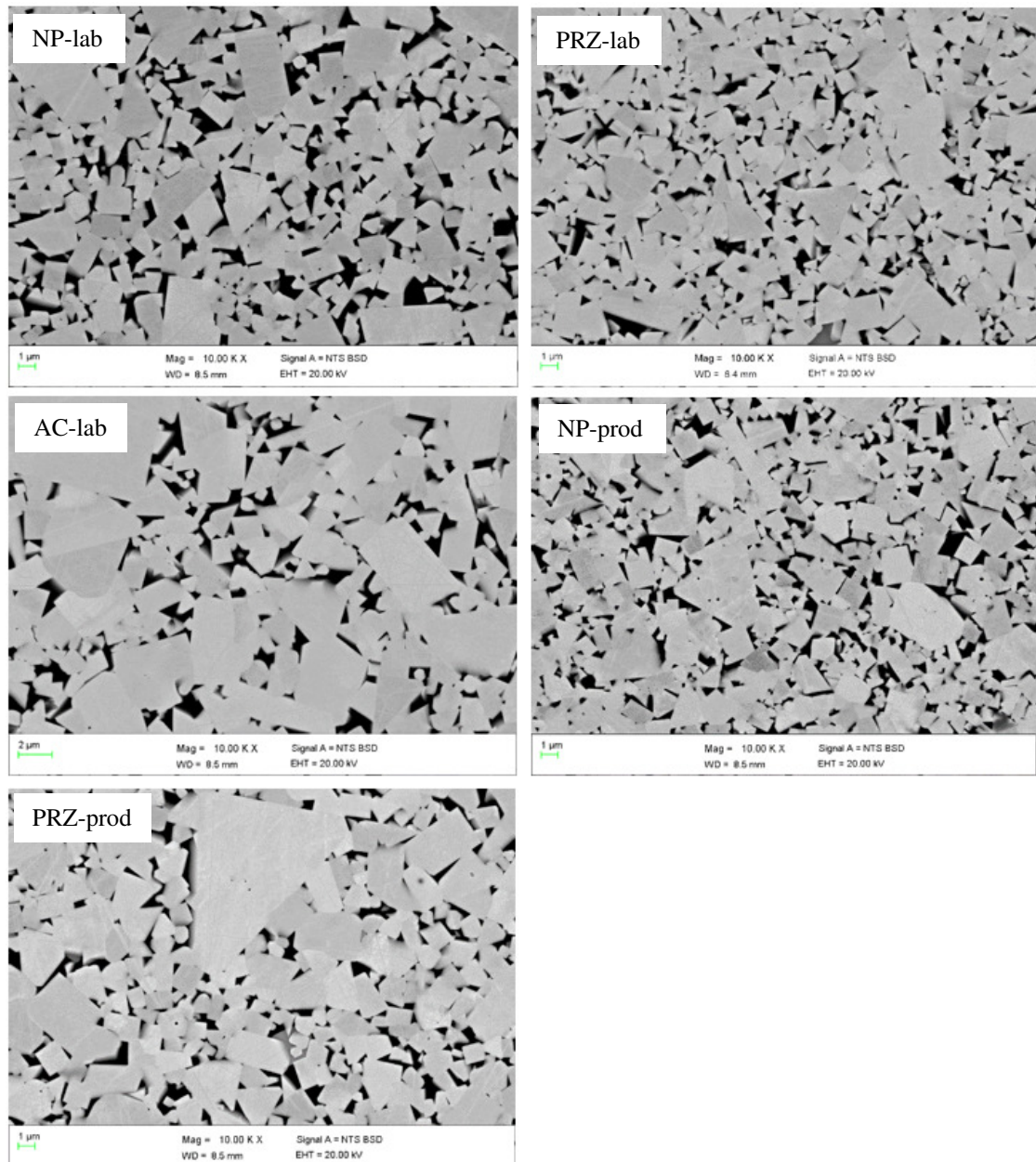


Figure 4-49 SEM micrographs of the sintered alloys at 10000X magnification in backscatter mode.

4.8.3 X-ray diffraction

The XRD patterns for the sintered grades are shown in Figure 4-50. Almost identical traces were obtained for all materials with prominent WC and Co peaks. No impurity phases were detected in the grades using this technique, which is likely due to their small quantities.

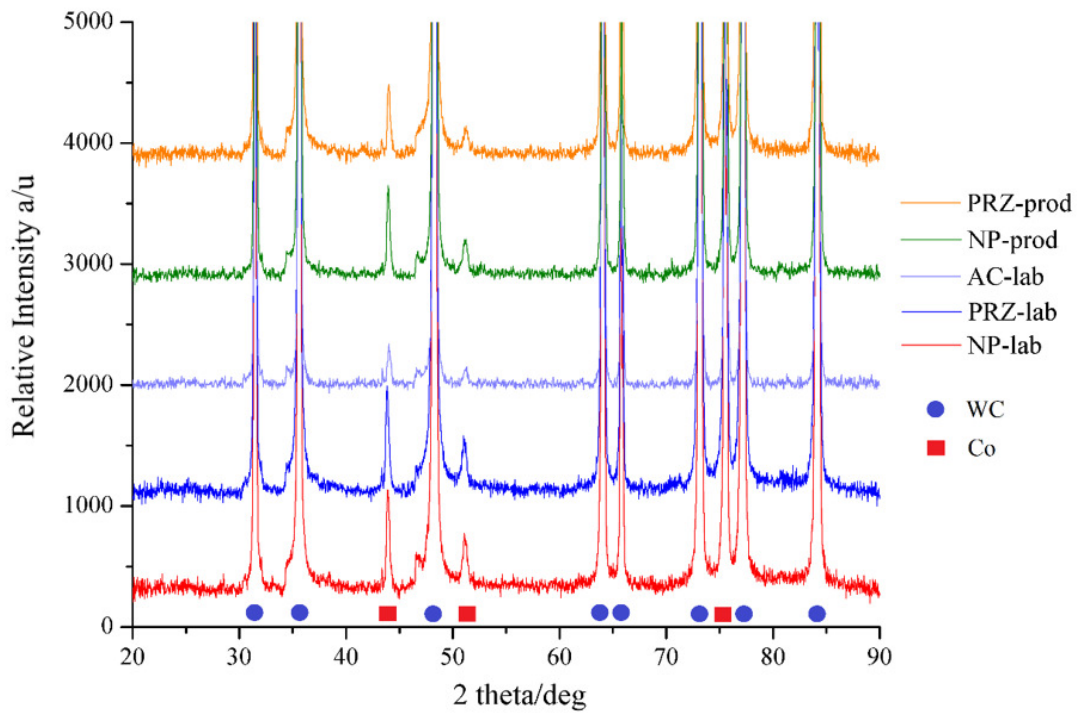


Figure 4-50 XRD traces of the sintered new, zinc recycled and acetic acid recycled materials, showing that WC and Co were the only phases present at detectable levels.

4.9 Metallurgical properties

Table 13 shows various material properties of the sintered alloys, with a benchmark value range which represents the ideal value for the specification of WC-6wt% Co mining material.

The magnetic saturation values for all materials, except two, were within the required benchmark value. PRZ-lab had a higher magnetic reading (6.4% as opposed to 6% or less), as did AC-lab. The coercivity and hardness are lowest for AC-lab, with the hardest and highest coercivity belonging to NP-lab and NP-prod. AC-lab and PRZ-lab fell outside the specification range for coercivity, but PRZ-lab was still within the required hardness range, unlike AC-lab, which was too soft. The density of the materials fell within the specification requirements, with the exception of PRZ-lab, which was slightly lower on average (it was only beneath the specification by 0.02g/ml).

Table 13: *Material properties of the sintered alloys.*

Grade	Magnetic saturation ($\times 10^{-7} \text{ Tm}^3/\text{kg}$)	Magnetic cobalt content (wt% Co)	Coercivity (Oe)	Vickers hardness (HV30)	Density (g/ml)
NP-lab	120.6 ± 1.7	5.85 ± 0.08	151.7 ± 1.2	1458 ± 9	14.94 ± 0.04
PRZ-lab	128.3 ± 4.2	6.40 ± 0.21	116.0 ± 1.7	1419 ± 8	14.78 ± 0.08
AC-lab	130.6 ± 4.1	6.56 ± 0.21	98.0 ± 2.0	1282 ± 7	14.88 ± 0.02
NP-prod	120.7 ± 0.8	5.86 ± 0.04	158.7 ± 1.5	1433 ± 15	14.85 ± 0.01
PRZ-prod	116.0 ± 4.0	5.52 ± 0.19	133.3 ± 1.5	1424 ± 8	14.97 ± 0.02
Benchmark	110 – 125	5.2 - 6.1	120 - 160	1350 - 1450	14.80 - 15.00

5. DISCUSSION

5.1 Introduction

The discussion first addresses the recycling processes and impurity characterization, followed by rheology, compaction behaviour and sintered material properties. A simple financial analysis is provided as the final discussion section, in which the industrial viability and costs associated with each powder production method are compared.

5.2 Zinc recycling process

The zinc recycling process was successfully carried out on the sintered NP-lab material, to produce PRZ-lab powder, as well as on recycled mining scrap which was used to produce PRZ-prod material (which is daily practise at Pilot Tools).

The patent for the zinc process recommended a soaking temperature range of 750°C to 850°C for 2 to 4 hours depending on the size of the scrap, followed by evacuation of zinc preferably around 800°C [4]. However the patent did not deal with a full scale production facility, hence the times and temperatures can be expected to be different when a large plant is used. The zinc recycling plant at Pilot Tools is of a customized design, in which the zinc was evacuated and distilled at 930°C for 36 hours, after previously soaking the WC-Co scrap in molten zinc at 930°C for 24 hours (the infiltration stage).

According to the Co-Zn phase diagram [87], at 930°C and above, Co-Zn forms a liquid phase at 72wt% Zn. As the wt% Zn increases, the temperature required to form the Co-Zn liquid phase decreases. A possible combination of a number of

Co-Zn solid phases + liquid co-exist at compositions from 38wt% Zn to 70wt% Zn, and below 38wt% Zn equilibrium favors solid α -Co formation at 930°C. The mechanism of zinc recycling makes use of the mutual solubility of Co and Zn [4] and the Co-Zn liquid phase that forms at high temperature (930°C in this study) when a sufficient amount of molten zinc is present. The patent states that zinc to binder (usually cobalt) weight ratio of the zinc process should be 10:1 up to 30:1 [4]. Unfortunately, it is not practical to measure the exact binder composition of a ton of scrap. Hence, a standard weight ratio is used, but this can lead to insufficient zinc infiltration if the scrap load is large, or high in cobalt, resulting in oversize material.

After the zinc process has completed, the entire recycled product is crushed to produce powder. It is difficult to distinguish oversize material from infiltrated material when the product is offloaded from the furnace, as the product emerges as a large ‘cake’ that is then broken down. The hard, non-crushable parts are only recognized as oversize material after crushing and are then separated from the powder. The cobalt content of the resulting powder can therefore be expected to be higher than that of the original scrap load if a significant amount of dense oversize material is present during crushing. This occurs because of the cobalt surface enrichment of only partially zinc recycled, dense oversize components. The cobalt rich (and zinc contaminated) surface layer is then broken off during mechanical breakdown and included in the resulting recycled powders, leaving the dense core behind, requiring a second recycling process to make use of it.

The oversize material is separated from the powder after crushing and dry milling. The powder is chemically analysed and used for further manufacturing, while the oversize requires either a second zinc recycling run, or can be used as feedstock material for the acetic acid process, as was done in this project. It was necessary to study the oversize material in order to improve understanding of the zinc recycling process, and to provide a baseline comparison for the oversize materials introduced into the supplementary acetic acid recycling technique. Both of which

could lead to subsequent improvements in the industrial production of carbide components using recycled powders

A SEM micrograph of the core region of the dense oversize sample was shown in Figure 4-4 (p 72), with the corresponding elemental micro-PIXE maps for W_L and Co. The micro-PIXE maps displayed a typical sintered WC-Co microstructure [88]. Figure 4-5 and 4-6 (p 73-74) showed SEM and micro-PIXE maps of the surface layers within the dense oversize material sample, and Figure 4-7 (p 75) showed the micro-PIXE line scans across the entire sample from the core to the surface.

Zinc concentrations fluctuated across the scanned region between 0 to 1wt%, indicating that most of the zinc was withdrawn from the sample by the zinc recycling process. Iron concentrations (not shown on Figure 4-7 as it overlaps with the Zn line scan) of up to 0.5wt% were detected by the line scan. Iron is a typical, major impurity in cemented carbides, as described elsewhere [88-90]. Comparing the Co and W line scans (Figure 4-7, p 75), cobalt increased steadily within the core, up to a value of approximately 20wt% Co. As the scan crossed the interface between the core and the layered structure, cobalt increased sharply to ~35wt%, in inverse relation to the W content. It was also noted that despite the core appearing dense, some porosity was observed in the SEM micrographs, and micro-PIXE mapping, where the total sum of the detected elements did not reach 100wt%, possibly resulting from the presence of porosity and matrix changes within the material, impacting the micro-PIXE results.

The withdrawal (by the applied vacuum and distillation process) of the zinc at 930°C extracted the liquid Co-Zn phase towards the surface of the material, resulting in the cobalt-rich region C, seen on Figures 4-5 and 4-6 (p 73-74). Region C (Figure 4-5) would therefore be expected to possess high porosity, once the zinc was evaporated; as confirmed in the SEM micrographs in Figures 4-5 and 4-6 (p 73-74). After the zinc content fell below 72wt% at 930°C (because of evaporation), several different phases formed as the zinc content progressively

decreased, until below 38wt% Zn (still at 930°C), when only solid α -cobalt (according to the phase diagram) remained. Deeper within the sample, however, less zinc infiltration occurred and therefore less zinc was available for formation of a liquid Co-Zn phase, hence less cobalt was extracted towards the surface by the vacuum, resulting in Region B, containing less cobalt than region C and a more finely layered structure. Region A (the sample core) had the lowest level (if any) of zinc infiltration, and consequently the cobalt in this core region did not form a liquid Co-Zn alloy phase at 930°C. Figure 4-7 (p 75) shows increasing cobalt content within the core (region A) moving outwards towards region B. Since neither liquid Co nor Co-Zn alloy formation was possible in the core (pure Co melts at 1495°C and the Co-Zn alloy could not form a liquid state with less than 38wt% Zn), this indicates that cobalt solid state diffusion occurred outwards from the core. Furthermore, the diffusion induced cobalt depletion may account for the porosity observed within the core. A significantly longer reaction time would be required to fully penetrate and embrittle dense oversize material as the dense core needs to be successfully penetrated.

A SEM micrograph and micro-PIXE maps of the porous oversize material were shown in Figure 4-8 (p 75). The porous oversize had extensive cracking, with SEM, micro-PIXE and the optical micrograph (Figure 4-3B, p 72), showing no clear cobalt gradients. Cobalt-rich clusters can be seen in the micro-PIXE maps, with some clustering occurring around the crack. Zinc levels less than 0.1wt% were detected in this sample, indicating that zinc was more successfully withdrawn from the porous oversize material than the dense oversize material, which fluctuated between 0 to 1wt% Zn. It is suggested that, despite zinc infiltration to the sample center of the porous oversize material, the cobalt clusters can still hold the material together strongly enough to prevent efficient mechanical breakdown, hence a slightly longer reaction time in the zinc recycling process would further weaken the WC-Co bonds in the porous oversize material, allowing for it to be broken down into powder.

The following explanation is offered for the difference between the formation of porous oversize and dense oversize material. Consider two identical masses of cemented carbide parts, one comprising larger diameter scrap and the other comprising smaller diameter scrap, and loaded with a constant mass of zinc prior to recycling. The small diameter samples possess a larger surface area to volume ratio compared to the fewer, large diameter scrap parts. The molten zinc, therefore, can penetrate the smaller diameter scrap more efficiently than the larger diameter scrap parts. As such, a more cobalt-rich Co-Zn melt is formed than if all of the cobalt is not fully dissolved in the Zn (in the case of the larger scrap parts). In the Co-Sn system [91], it was shown that the viscosity of the molten Co-Sn increases with an increase in the amount of cobalt (the higher melting point metal) present in the melt. In the current study it is therefore suggested that the Co-Zn system behaves similarly, with higher viscosity Co-Zn forming in the case of smaller scrap parts (Co-rich), and lower viscosity (Zn-rich) melts forming in the case of larger scrap that is not fully zinc infiltrated. The more viscous Co-Zn melt can therefore better resist flow under the force of the vacuum, restricting Co migration to the surface. Zinc removal proceeds by evaporation and local re-precipitation of the cobalt and consequently porous oversize material forms. Whereas, the lower viscosity (Zn-rich) Co-Zn melt can migrate towards the sample surface under vacuum, hence forming the observed cobalt gradient structure as the zinc evaporates and the cobalt is deposited, resulting in a dense oversize material sample as described earlier.

Based on the results of this study it is therefore recommended that correct sizing of WC scrap components prior to the zinc recycling process, as well as optimization of the soak and distillation times, could result in less cobalt variation within powders and less zinc contamination.

5.3 Acetic acid recycling

The acetic acid plant was constructed and operated successfully, producing a significant quantity of recycled powder. After 3 weeks of operation, some dense oversize material remained, but the extracted powder was successfully used to produce a batch of AC-lab material for further study.

The leaching rate of the acetic acid run was rapid initially but slowed down with time, requiring further top-ups with acid to promote further leaching. This result is consistent with Edtmaier et al. and Meissl [3, 6, 7] who reported the same phenomenon on fully dense components. The acetic acid selectively attacks the cobalt and not the WC grains when leaching [3]. This is because cobalt belongs to the reactive ferrous metals group of elements which are easily attacked by acids. Tungsten carbide, which has a ceramic nature with strong interatomic bonds, is more acid resistant. The exposure of new cobalt surfaces to the acid depends on the removal rate of the cobalt, via the binder mean free path. In the cemented carbide industry, the binder mean free path is a term used to describe the distances between the interconnected network of cemented carbide particles, held together by the metal binder (cobalt usually), which depends on the grain size and microstructural characteristics of the material in question [92]. The grain size and cobalt content of the material can affect leaching rates. It has been previously demonstrated that a finer grain size hampers the diffusion of oxygen and acetic acid to the unreacted cobalt within the microstructure, conversely more cobalt increases the rate of leaching [3, 7]. Furthermore, as the binder is removed and the acid penetrates deeper within the sample, it is reasonable to deduce that the reaction rate will decrease, because of the increased time required for fresh acid to diffuse into the sample and for the acetate ions to escape into the ‘free liquid volume’ within the reaction vessel, carrying the cobalt with it. As such, it is expected that reaction rates would drop with time, despite sufficient acid and cobalt present within the system to continue the reaction.

The leaching rate is dependent on available surface area for reaction. Hence, the large exposed surface area of the PRZ oversize material explains the extremely rapid initial reaction rate of the acetic acid leaching process (Figure 4-9, p 77). A large amount of exposed cobalt was in contact with the concentrated acid, after which the reaction rate reduced. In essence, the oversize material behaved like a sponge by containing a large volume of acid, with many surface sites available for reaction.

Figures 4-10 to 4-12 (p 78 - 80) show the SEM micrographs and micro-PIXE maps of the fully dense, sintered WC-6wt% Co cylinders that were exposed to the acetic acid. The leached layer was only 700 μ m thick even after the 21 days of leaching. An abrupt termination of the leached zone occurred at the interface with the un-leached core, the interface being approximately 10 μ m thick at most (shown by the SEM images and micro-PIXE maps of Figures 4-10 to 4-12). The average sintered grain size of these cylinders was approximately 3-5 μ m. Recall that NP-lab material was used to produce these cylinders (see Figure 4-48 and 4-49 (p 144 - 145) showing its microstructure), hence indicating that the acid was only able to penetrate about 10 μ m into the material ahead of the main acid leaching front (via the binder mean free path) in some places if the cobalt pools were interconnected, but typically had to leach out each cobalt binder pool layer one at a time in the sintered material.

The acetic acid leaching of the oversize samples depended on the nature of the oversize material. Porous oversize (Figure 4-13, p 82) was rapidly leached of cobalt within ten days, leaving behind a cemented carbide skeleton structure that was easily broken down. It was also observed that some of the oversize extracted during the first few days of the experiment, spontaneously broke apart upon removal of the sample from the reactor - indicating that leaching had progressed sufficiently to reduce the material to powder with little applied force. It is suggested that such instances occurred with porous oversize material that was rapidly acid infiltrated and leached.

The dense oversize material, however, remained largely intact (Figure 4-14, p 83), where the surface of the samples resembled those of the sintered samples during leaching (Figures 4-10 to 4-12, p 78 - 80). Since it has been shown that dense oversize material possesses a porous, cobalt enriched surface it can be concluded that the acetic acid attacked and removed this layer within the 21 days - since this layer was not visible in any of the extracted dense oversize material samples. The removal of the cobalt enriched zone was assisted mechanically by the bubbling action of the acid bath which was quite rapid, creating turbulence within the liquid, as well as readjustment of the scrap metal bed under its own weight. Hence, in the case of dense oversize material, the dense core was left behind to leach as sintered material does - at a much lower rate of reaction. Since the overall powder yield of the experiment was only 60%, the remaining 40% remained behind largely in the form of the cores of dense oversize material that had only been partially leached.

The micro-PIXE maps of all of the leached samples showed removal of the alloying metals in the cobalt binder such as Fe, Ni and Cr. Although this is not a unique finding [3] it presents a concern should the acetic acid technique be used to recycle the cobalt industrially, as it will need to be purified in a separate step, or will contain these elements in increasing quantities if the material follows several recycling product lifetimes.

5.4 Impurity characterization

The accurate detection of impurities in cemented tungsten carbides is important because impurities influence the production, quality and performance of hardmetals. Several techniques were used to detect the levels of impurities in the different WC-6wt% Co grades, which are presented first, followed by a critical comparison of the techniques.

5.4.1 Determination of impurities

The preliminary investigation using micro-PIXE as a characterization method in powder metallurgy, with a focus on granulated powders, revealed that despite pre-recycling sorting methods, some elements typically associated with tool grades were detected, such as Ti, Ta and Nb. Titanium should not be present at all in a 'straight grade' (SG), yet was detected in substantial quantities (0.13wt%) by the micro-PIXE scans. Titanium was well distributed within the tool grade (TG) and recycled straight grade powders alike, demonstrating that a satisfactory production process was employed in order to homogenize the powders. However scrap sorting presented a demonstrable problem to the cross contamination of zinc recycled materials. The level of Ti present in the alloy may alter the performance of the recycled SG products and ultimately the performance of the tool, and hence needs to be controlled wherever possible [19].

Iron contamination from recycling and powder processing respectively was observed. Iron was detected in both the straight grade (0.21wt%) as well as the tool grade material (only 338ppm), and likely originated, at least in part, from ball milling using stainless steel ball mills in manufacturing, the same applies to nickel. Up to 0.3wt% Fe can completely dissolve in the binder phase and recycling and milling have previously been identified to contribute to this [90]. At low binder (cobalt) concentrations, iron can modify the mechanical properties and wetting properties of the binder phase [90] hence, its accurate quantification is necessary. Trace elements Cr, Cl, Ca, and S were detected in the straight grade but not in the tool grade powder, demonstrating impurity pickup associated with recycling of used tools. Chromium could have originated from the ball mills (along with Fe and Ni) but Cr is also used as a grain growth inhibitor (up to 0.15wt%) in some WC based materials [90, 93]. Calcium contamination (50 to 100ppm) can originate from lamp black (primarily carbon powder added to adjust the stoichiometry of the batch), Co powder (~150ppm) and from environmental dust [90]. If S is present, the stable CaS phase can form that gives rise to brittle phases and porosity. The presence of sulphur can originate from lamp black (up to

0.5wt%) and can also be introduced by recycled powders [90]. Sulphur content has been exclusively detected by combustion analysis methods in the past and questions have arisen as to its accuracy [90], further attributing the value of micro-PIXE as a complimentary technique. Prior to the zinc recycling process, a hydrochloric acid mixture is typically used to clean the scrap hence it is possible that the chlorine content arose from this process.

To ensure the quality of the final product and the required standard of material, impurity levels need to be quantified and controlled. Micro-PIXE has previously been used to identify the reason for the formation of corrosion pits in sintered WC based materials, with trace elemental contents too low for detection by scanning electron microscopy [94]. The current investigation demonstrates the use of micro-PIXE in powder metallurgy characterization, for example the milling process can be optimized to reduce Fe/Ni contamination etc., by comparing results after a process change. Furthermore, it can be seen that micro-PIXE can detect both major constituents and contaminants down to ppm levels of accuracy, and hence was suitable for a detailed analysis of the recycling methods studied later in this work.

The same impurities were found in all of the studied grades, with the overall impurity levels being low. From the ICP-OES data (Table 5, p 87), it can be seen that W, C and Co account for greater than 99wt% purity in each grade. The significant impurity differences between the grades correlated to the level of each impurity detected.

The impurity which showed the highest level for each grade, irrespective of identification technique used, was Fe contamination. According to Ortner and his collaborative study between major manufacturers [90], the impurity levels detected in these materials are acceptable, except for Fe in grades PRZ-lab and NP-lab, which were atypically high; less than 0.3wt% is considered normal. High iron content can have a negative effect on mechanical properties and wetting properties of the binder phase. The Fe content was highest in grade PRZ-lab,

followed by grade NP-lab and then grade AC-lab. The micro-PIXE analysis (Figures 4-17 and 4-18, p 90 - 91) clearly showed the high iron concentration within powder PRZ-lab compared to the other grades, with large clusters of Fe heterogeneously distributed throughout the powder. The high Fe content of grades PRZ-lab and NP-lab is likely due to the milling procedure used for these two powders. The same applies for AC-lab which had acceptable Fe levels of around 0.3wt%.

The ideal mill load for the 'lab' mills used in this work is 120kg but for this project 50kg of powder was milled due to high material cost and material availability, hence the mill was not fully loaded which could cause increased wear of the stainless steel mill lining, or reduce the dilution of the impurities in a large volume of powder. This would also account for the higher levels of, especially Cr and to a lesser extent Ni, detected in these two grades compared to grade PRZ-prod, which was milled at full capacity in a larger mill. The higher Fe levels in grade PRZ-lab compared to grade NP-lab, is due to grade PRZ-lab being produced from recycled grade NP-lab alloys. From the SEM-EDS and micro-PIXE analysis there is a correlation between the Fe contamination and the Co binder pools, indicating that Fe forms part of the binder phase. Iron is known to undergo complete dissolution in the Co binder phase unless the Co content is low and the heterogeneous Fe particles are large [90].

The presence of Ti, Ta, Nb, V and Zn (detected by ICP-OES, Table 5, p 87) in all of the grades is due to the use of commercial production processes to produce the materials for this study. These elements are not inherently present in the original powders. Grade PRZ-prod had higher levels of Ti and Ta than the other grades. This is attributed to the inadequate separation of the mixed carbides present in the recycled mining scrap material used to produce this grade. Zinc levels were low in all of the recycled grades, indicating successful PRZ vacuum and distillation operation. The low levels of Ca and Cu found in the grades is considered to be typical for the raw materials used for the production of cemented carbides [95], however AC-lab possessed higher copper levels, likely originating from the braze

material used to secure mining components to stainless steel mining bodies. Some braze material can remain bonded to the carbide tool after removal of the spent cemented carbide part from the mining drill. This material is usually removed by aqua-regia acid washing, but occasionally some stubborn adherent braze (copper containing) material is overlooked or insufficiently removed during the scrap washing process, and is subsequently introduced into the powder. The increased Cu level in the micro-PIXE analysis, however, is believed to predominantly result from the copper-containing resin used for sample preparation, as it is not present in the ICP-OES analysis in significant quantities in the other powders. Grades NP-lab and NP-prod, which were new powders, had several impurities in low amounts; some were inherent in the original powders while others were picked-up during production. When NP-lab was sintered and then recycled using the zinc reclamation process to produce grade PRZ-lab, the level of all the impurities increased which is attributed to both the zinc recycling process as well as the commercial production methods used to produce this grade.

A comparison of the microstructures revealed that the recycled mining scrap grade, PRZ-prod, had the most homogeneous Co distribution, in both powder and sintered form (see Figures 4-17 to 4-20, p 90 - 94 and Figures 4-45 to 4-46, p 140 - 141). No distinct Co-rich or Co-poor areas were found in this grade. This high level of homogeneity is attributed to the increased levels of crushing and milling to which this grade was subjected (due to previous product life cycles), as well the powerful commercial production mill used. AC-lab was moderately homogeneous in terms of cobalt distribution, because 4.5wt% of the cobalt remained despite acetic acid leaching, hence the cobalt in this grade was subjected to processing a second time, improving overall homogeneity, and only 1.5wt% of new cobalt was added to correct the batch composition. Grade NP-lab and NP-prod, produced from newly purchased powders, had the least homogenous Co distribution (see Figures 4-19 and 4-20, p 93 - 94), showing large Co agglomerates within the powder which formed large Co pools in the sintered microstructures (Figures 4-45 and 4-46, p 140 - 141). The differences in homogeneity were detected in both the SEM and micro-PIXE analysis; however a clearer distinction between the grades

was observed using micro-PIXE analysis. This is in contrast to the results of Karhumaa and Kurkela [5] who reported no differences in the Co homogeneity between their new and zinc-recycled hardmetals using SEM investigations. Perhaps such effects are not always visible, depending on processing and analysis methods and the volume of material sampled i.e. micro-PIXE has better depth penetration than SEM (discussed later).

From these results, it is evident that PRZ-prod possessed greater homogeneity than the other powders (and to a lesser degree, so did AC-lab), showing no distinct cobalt rich or poor areas at all, in contrast with the new powders. The laboratory milled powders also displayed superior homogeneity of the recycled powders compared to the new powder, but not to the same extent as PRZ-prod.

5.4.2 Comparison of the analytical techniques

The grades were carefully manufactured as WC-6wt% Co powders. Despite this, the detected Co levels were similar however, but not the same, for each grade. Micro-PIXE analysis extracted from the maps shown in Figure 4-17 and 4-18 (p 90 - 91), indicated that grade NP-lab had 7.56wt% Co, PRZ-lab had 5.31wt% Co, PRZ-prod had 6.66wt% Co, AC-lab had 6.91wt% and NP-prod had 7.27wt% Co. Conversely the ICP-OES data detected approximately 6wt% Co in each grade. These differences between the two detection methods is that the micro-PIXE data is largely the result of the proton beam depth penetration, detecting a heterogeneous elemental distribution within the granule, which is microstructure specific, while the ICP-OES method, using acid digestion prior to analysis, reported more batch specific Co content (at expected levels of 6wt%). However, comparing the overall micro-PIXE map concentrations of the sintered bodies (Figures 4-45 and 4-46, p 140 - 141), the overall Co distribution can be seen to be approximately 6wt% throughout the entire sintered body, showing a good correlation between the two methods, and confirming that the grades had the required binder amount.

The structural dependence of the micro-PIXE mapping and quantification is further demonstrated by comparing the powder micro-PIXE maps of the grades in Figures 4-17 and 4-18 (p 90 - 91) to the data listed in Table 6 (p 92). Taking the $\text{Co} / (\text{Co} + \text{W})$ percentage of each extracted region numbered 1 to 5, in Figures 4-17 and 4-18, gives NP-lab: 7.78%, PRZ-lab: 7.23%, AC-lab: 7.72%, NP-prod: 8.30% and PRZ-prod: 6.90%. These ratios are within about 1% of each other, while the data reported in Table 6 shows that the W signal for grade PRZ-lab is only 68.13% of the composition, compared to 80-90% for all the other grades. Clearly this is impossible in terms of the actual composition of the batch, but rather represents a significant deviation from the expected W weight percentage of the batch; approximately 88.2wt% W for a pure WC-6wt% Co alloy. A possible cause for this deviation could be a microstructural feature. For example, an occluded micro-void within the powder granule, concealed by the powder around it, which is invisible to the operator when selecting a region for mapping. This effect was confirmed by selecting a variety of areas for mapping from the same granule which revealed that the W signal strength varied between 75% and 93%. Therefore care has to be taken when using micro-PIXE to analyse microstructures (especially powders). This method requires a large powder sample volume, with careful sample preparation which includes polishing of the powder. Furthermore, micro-PIXE is susceptible to beam shadow effects if a 3-dimensional object such as a spherical granule is analysed without cross sectioning, and porosity that may appear as material-deficient (darker) regions.

Ortner [90] compiled an extensive report on the influence of trace element impurities on hardmetals using a range of analytical tools. However the use of proton induced x-ray emission (PIXE) was not considered. In the current study the use of micro-PIXE to quantify the impurities in cemented carbides produced from new and zinc recycled powders has shown this method to be an effective characterization tool. Micro-PIXE can be used to distinguish homogeneity of major and minor elements within spray dried powders, providing a visual account and fully quantitative elemental distribution deep into the granule, allowing for a better understanding of powder production. Micro-PIXE has an advantage in that

it is capable of visually, quantitatively mapping both powder and sintered structures, as well as allowing for quantification of the elements before and after sintering. In terms of powder elemental analysis, both ICP-OES and micro-PIXE provide the capability for accurate quantification, especially in the case of major elements, with care needing to be taken because of structural effects (such as occluded voids – see page 54) when using micro-PIXE, while ICP-OES would require a smaller sample volume but thus demanding a highly homogeneous material for accurate analysis of a large batch to be reported. Furthermore ICP-OES and carbon-sulphur analysis requires a binder-burnout step using a furnace to remove the polymers used in powder production, while micro-PIXE is capable of powder analysis in the spray dried condition to examine the granule microstructure, as well as elemental composition. Although both ICP-OES and micro-PIXE can detect elements down to ppm levels of accuracy, micro-PIXE can detect their distribution within the sample and their relationship with other elements.

XRD analyses of the powders, detected none of the impurity phases, not even iron, the most significant contaminant, and is therefore unsuitable for contamination studies at these low impurity levels. The major elements, namely W, C, and Co were detected by EDS, with Fe being the only impurity observed on the EDS scans.

Depth penetration or bulk volume of the material sampled by the analytical techniques studied in this work (XRD, micro-PIXE, SEM and ICP-OES) is of importance when comparing the methods and their results. When using XRD, the depth penetration of the X-rays into the WC-Co samples was calculated at approximately $3\mu\text{m}$, using the mass absorption coefficient of W, copper radiation with a wavelength of 1.542 Angstroms and a photon energy of $2 \times 10^{-2} \text{MeV}$ [96]. Micro-PIXE depth penetration was calculated as approximately $28\mu\text{m}$ for 3MeV protons using the theoretical density for a WC-6wt% Co alloy, calculated using the SRIM software package. Using the Kanaya-Okayama equation [97] for calculating electron beam depth penetration in the SEM, the result for a W-rich alloy at 20keV

accelerating voltage, is less than 1 μ m. As mentioned before, the ICP-OES sample mass is very small, depending heavily on batch homogeneity for accuracy. Figures 4-45 and 4-46 (p 140 - 141) show circled, numbered regions 1 to 4 (on the cobalt distribution maps) which indicate regions where micro-PIXE detected a higher cobalt content (circle 1 & 2) and a lower Co content (circles 3 & 4) in the sample volume. This can be explained using the principle shown in Figure 5-1 (on the following page) which illustrates a proton (PIXE) beam as it intersects different sample volumes. During the micro-PIXE scan, the proton beam rasters across the sample surface, sampling a volume of the material by emitting X-rays which are detected and converted into data, up to 28 μ m deep from within the sample volume. If the beam encounters a volume such as that indicated in Figure 5-1 by beam position 1, and thereafter samples an adjacent volume (position 2), if the beam path intersects more cobalt pools through the volume in position 1 than position 2, the micro-PIXE map will report a low cobalt region adjacent to a higher cobalt region projected onto the resulting two-dimensional micro-PIXE map. Hence, micro-PIXE is highly sensitive to the volumetric homogeneity and binder mean free path of the materials because of its farther depth penetration capability, making it a superior analytical tool for homogeneity determination in cemented carbides.

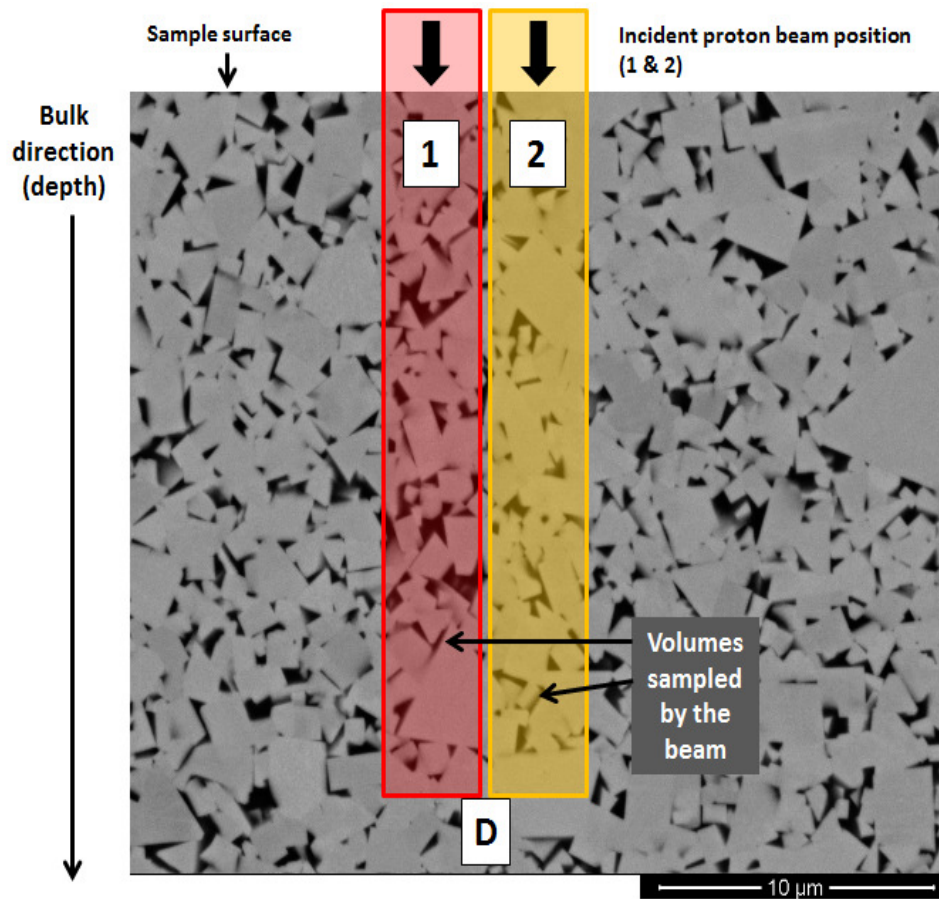


Figure 5-1 Illustration of micro-PIXE beam depth penetration cross section through a WC-6% Co alloy. 1: First beam position, the beam intersects a sample volume rich in cobalt. 2: Second beam position, the beam intersects a sample volume with less cobalt (more WC). D indicates the maximum depth penetration of the beam capable of exciting detectable x-rays.

5.5 Milling

The milling curves showed that the new powder (NP) milled considerably faster than both recycled powders and the acetic acid powder milled slightly faster than the PRZ powder. From the SEM micrographs of the new powders, Figure 4-23 and 4-24 (p 97 - 98), the round and agglomerated nature of the grains was evident which is in contrast to the PRZ and AC powders which showed a broader particle size distribution. Dense, angular grains were present in these powders. Karhumaa

and Kurkela [5] also found that their PRZ powders exhibited a broader particle size distribution, which they attributed to the agglomerated nature of the WC and Co grains resulting from the PRZ process [5]. In an attempt to explain the different milling rates, additional high magnification SEM of starting materials before milling, were performed, shown in Figure 5-2, on the following page.

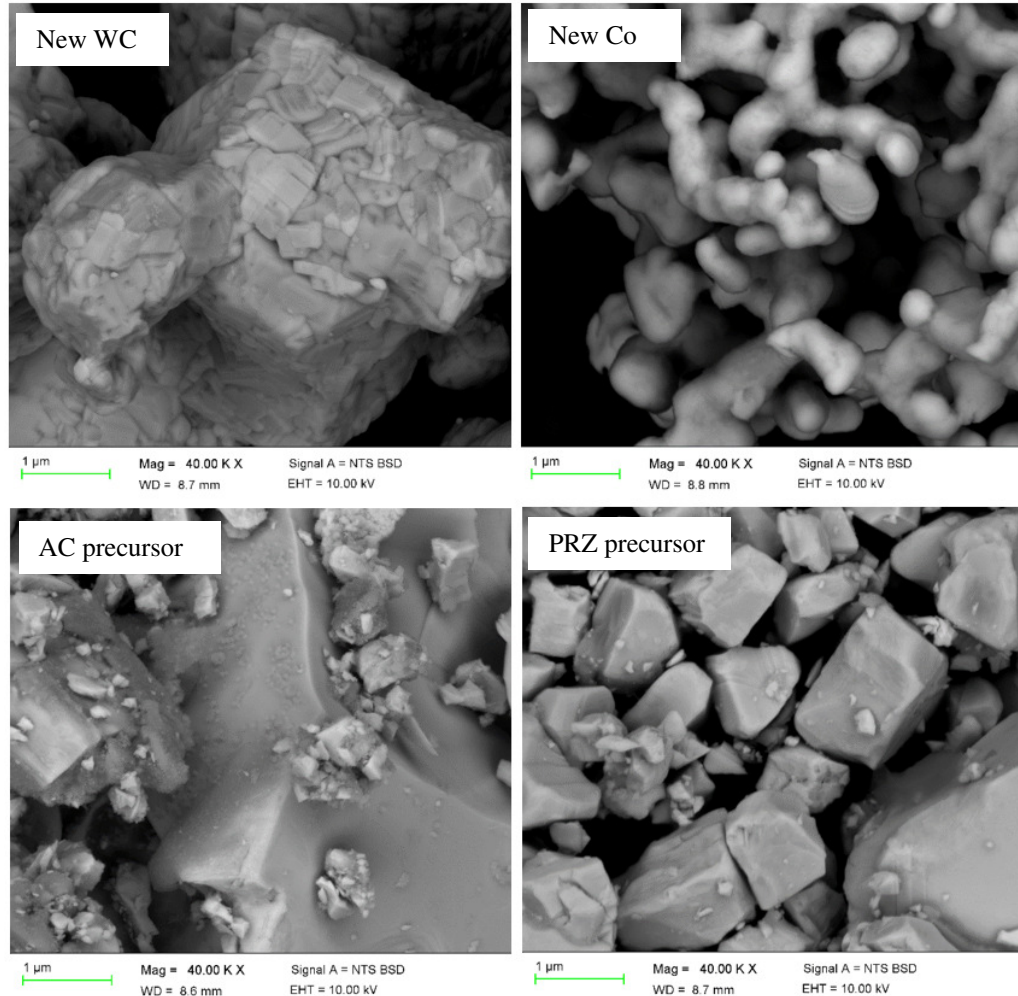


Figure 5-2 Scanning electron micrographs of the starting powders for each milling experiment at 40000X magnification.

The new WC powder (Figure 5-2) shows a grain composed of many crystallites with defined crystallographic boundaries and orientations. It is expected that these crystallites can easily break off during milling, as there are many ‘faults’ and visible crack initiation points. Additionally, the cobalt powder was extremely

finely divided, possessing many 'necks' or weak points which would allow for easy mechanical separation during milling. Hence, both constituents of new or 'virgin' powders appear to favour a rapid milling rate. The AC and PRZ powders, however, possessed some very large grains which displayed evidence of brittle fracture i.e. sharp fracture points (due to dry milling subsequent to zinc recycling) as well as some cobalt still adherent to the WC. Aside from the wider grain size distribution of the recycled powders, they also comprised a fraction of very large grains that were not broken down during mechanical breakdown of the PRZ 'cake' into powder. The PRZ and AC grains showed no evidence of 'weak spots' or crystallite boundaries in the same way as the raw WC material did. Therefore, fewer 'easy' crack initiation and propagation points existed within the previously sintered grains, and as such, were more difficult to break down during milling than the new powders. Additionally, the presence of larger grains of previously sintered cobalt in the PRZ material (and not freshly added cobalt as in the case of the new powder and AC material) can also be expected to increase milling time of PRZ material compared to material containing fresh cobalt. An example of a Co covered WC grain from the PRZ material is shown in Figure 5-3.

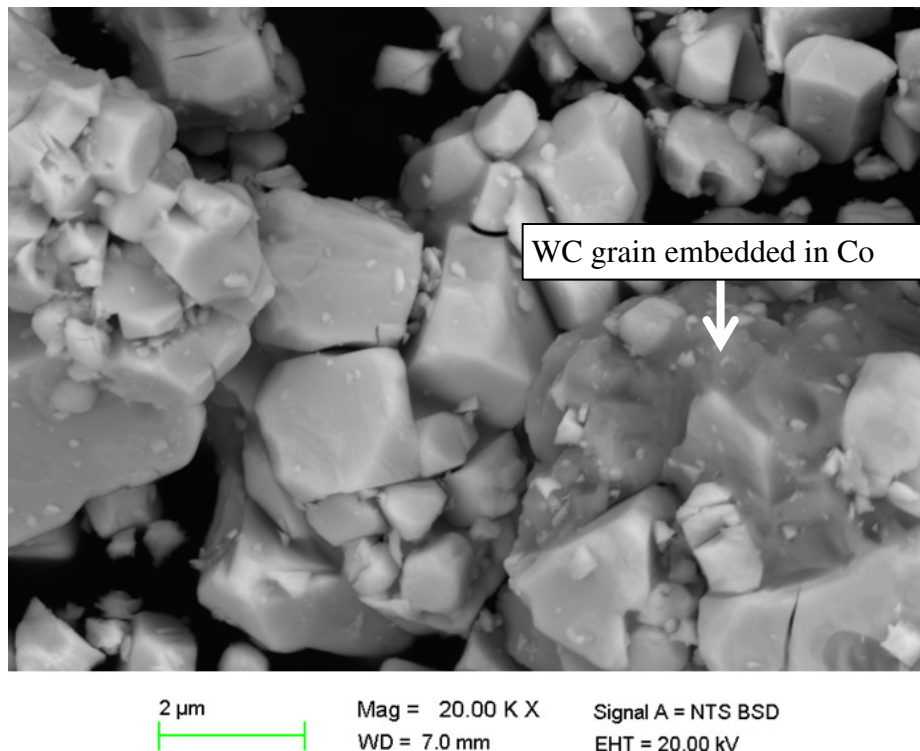


Figure 5-3 SEM micrograph of a WC grain encapsulated in cobalt after completion of the PRZ process and dry milling, at 40000X magnification.

On the basis of Rüdiger et al's [98] description of the different Co binder mechanical properties, it is suggested that the properties of the binder could affect milling behaviour and milling rates, since milling relies on the fracture and deformation of the powders. For example, zinc recycled WC-Co materials were previously sintered before recycling, hence the cobalt binder contains dissolved elements, especially tungsten, which can alter the mechanical properties of the cobalt [98].

The SEM micrographs of the milled powders confirmed the results of the particle size analysis. The new slurries had the most consistent overall particle size that broke down quickly and consistently. In agreement with the results of this study, Karhumaa and Kurkela [5] noted that after extended milling in a laboratory ball mill, the particle size distribution of the zinc reclaim powder could be made almost identical with that of new powders. Cobalt mapping (using SEM and EDS as shown on page 18) confirmed that cobalt was well distributed in the zinc reclaim

powder after wet milling. They concluded that, despite possessing agglomerates, the PRZ material could be broken down to the required size [5]. In this respect, the results of this study agree with, but expand upon, their work by further investigating the properties and production implications of using PRZ and acetic acid recycled materials.

5.6 Slurry rheology

In this section of work, an attempt was made to understand the fundamental rheological properties of the WC-6wt% Co powder slurries produced by the zinc reclamation and acetic acid recycling processes, compared to the new (virgin) material equivalents. Factors that were taken into consideration included milling behaviour, particle size, solids loading, zeta potential, viscosity, settling rate and polymeric binder condition. The effect of these factors on the slurry rheology is discussed below.

5.6.1 Polymer integrity

Polymer additions fulfill various roles in powder metallurgy, but most importantly, they are added as binders and lubricants to facilitate the compaction process. Previous studies have shown that the viscosity of polyethylene glycol solutions increases with increasing molecular weight of the polymer [99, 100]. Hence, if the polymer were to break down during milling, the viscosity of the slurry would change and consequently could impact the quality of the spray dried powder. It would also render comparisons of the slurry rheology of the various slurries inaccurate, therefore justifying an investigation into this issue.

The polydispersity index (PDI) is a measure of the polymer molecular weight distributions [101]. To make a correct evaluation of the PDI's the number (M_n)

and weight (Mw) average molecular weights must be considered [101]. From Table 8 (page 111) it is clear, that these values were very similar for all the extracted polymers from the different powders, despite varying milling times. PRZ-lab was milled for 26 hours compared to NP-lab's 14 hours, and yet the difference in the Mw and Mn values is only 4.5%. The PDI's for the polymers were similar, indicating that milling time, under the conditions of this study, had no effect on the integrity of the polyethylene glycol based binder system. Consequently, polymer breakdown did not occur and therefore does not contribute to rheological differences in the slurries.

5.6.2 Rheological interpretation

The properties of cemented carbides are dependent on the properties of the carbide phase, the properties of the Co binder phase and the interaction between carbide and binder [98]. During sintering, W and some C, diffuse into the Co binder phase. The amount of W in solution depends on the C content, the grain size, the Co content, as well as the sintering and cooling conditions [98]. In terms of the new powders, fresh Co and fresh WC were introduced into a mill and homogeneously mixed to produce the required slurries. The zinc recycled powders were different from the new powders, because they were already been sintered and broken down again mechanically after recycling. Since zinc recycled materials contain WC and Co grains that are separated by the recycling process, the W and C remains in solution within the Co binder in the recycled powders. Therefore, the properties of the recycled Co binder are different from those of new powders. SEM micrographs of the dried slurries (Figure 4-34, p 119) show that with PRZ-lab material (100% zinc recycled powder) the Co binder phase is more difficult to distinguish (at the same brightness and contrast setting) compared to the new powders (NP-Prod and NP-lab). This is because the binder is alloyed with W, and thus has a higher atomic weight and appears lighter in contrast, in response to the electron beam, than a pure Co grain of lower atomic weight. The differences between pure Co and zinc recycled Co, could contribute to the differences observed between the

slurries, including the trend towards consistently more favourable zeta potentials (all greater in magnitude than -16mV) for the PRZ materials comprising WC and alloyed Co, compared to the new materials comprising of WC and pure Co. Furthermore, not all of the Co is separated from the WC grains by the zinc recycling process and milling operations. Figure 5-3 (p 167) shows a SEM micrograph of zinc recycled powder, where WC grains are encapsulated in cobalt binder, despite milling. Hence, the PRZ slurries contain WC particles with some adhering Co binder, while the new powders contain discrete WC and Co grains.

The grain size effects on slurry rheology can be better appreciated by plotting the final slurry viscosity measured at high solids loading (11.6wt% ethanol, at 500s^{-1} shear rate) against the mean volume grain size distribution, as shown in Figure 5-4.

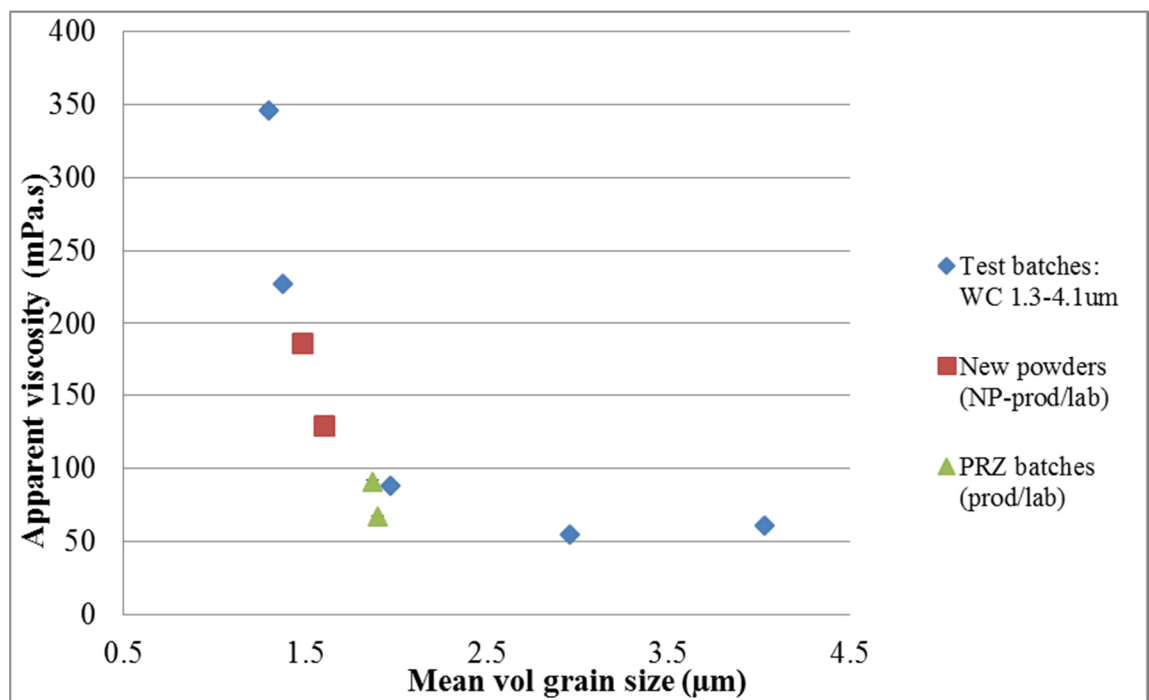


Figure 5-4 Final viscosity (at a shear rate of 500s^{-1}) against mean volume grain size for the new powders and WC test batches of varying grain size, with the PRZ batches overlaid.

The slurries followed a trend of exponential viscosity increase with decreasing grain size. Other researchers [65, 102] have found similar results on different slurry systems, attributing this behaviour to strong interactions holding the particles together in the slurry and immobilizing some of the liquid medium between them. This effect increases as the particle size decreases and consequently surface area of the particles increases. The smaller inter-particle distance provides an increased attractive potential and a larger probability of collisions between particles [65, 102]. A larger shearing force is required to overcome the internal friction between the particles, allowing the slurry to flow. Consider the behaviour of slurries WC-1.3 μm and WC-1.4 μm . When the SEM micrographs of these powders were compared in Figure 4-32 (p 116), WC-1.4 μm had a finer WC grain size than WC-1.3 μm , yet the measured grain size distributions present the opposite result, as indicated in Table 9 (p 112). The SEM images showed that WC-1.4 μm contained tightly packed agglomerates that were larger than the individual grains of WC-1.3 μm . Yet, the slurry rheology of this powder and the measured particle size distributions, indicated that this powder slurry behaved as if it were composed of coarser particles. The agglomerates were not sufficiently broken down in the small laboratory mill, and so, acted as larger particles both in terms of particle size analysis (despite 2 minutes of 40W ultrasound) and rheological behaviour. Hence, this demonstrates that agglomerated slurries behave, rheologically, like slurries of a coarser grain size, if the shear stress is insufficient to break down the agglomerates.

It is well known that the zeta potential, and hence the state of dispersion, of slurries is closely related to the rheological behaviour [58, 65]. The zeta potentials of the various slurries range from close to zero to a magnitude of around 30mV. A zeta potential (positive or negative) of less than 10mV is indicative of strong aggregation tendencies, 10 to 20mV is considered an unstable dispersion, and 30 to 50mV is considered incipient stability. A zeta potential greater than 50mV indicates good particle stability within a slurry. Zeta potential is highly dependent on the state of the charge double layer that surrounds a particle in suspension, and on the potential determining ions, for example H^+ and OH^- that are in solution, and

the pH of the suspension [65]. In this work, the stability of the slurries was measured at the pH of pure ethanol, i.e. the solvent system used to mill and spray dry the slurries. The surface properties of slurry particles are easily changeable with changes in specific surface area, solubility of fine particles, reactivity, heterogeneous surface chemistry, and degree of oxidation [65]. The new powder slurries of WC-1.3 μm to WC-4.1 μm displayed a wide range of zeta potentials and no clear relationship with grain size. The grain size of the particles in this study was orders of magnitude larger than the separation distance of molecular ions in solution. Zeta potential is dependent on the difference between the particle surface charge and that of the outer Helmholtz plane [65]. The dimensions of the diffuse charge double layer surrounding the particles is much smaller than the particle size, therefore it is unsurprising that zeta potential did not clearly depend on grain size for the particle size range studied in this work. Surface effects of the particles, the oxidation state and surface chemistry, which can vary from batch to batch, are expected to affect zeta potential more than grain size. Furthermore, since the grades WC-1.3 μm to WC-4.1 μm were made from different batches of different starting particle sizes, in order to study the effects of particle size on rheology and explain the results of this study, the surface chemistry could not be kept constant. Nevertheless, the rheology results confirm a direct effect of grain size on rheology, despite variable zeta potential; therefore, grain size effects are dominant over zeta potential in these slurries.

All the WC-6wt% Co slurries exhibited dispersions that tended to agglomerate, with the greatest degree of zeta potential variation experienced by slurries produced from starting materials of differing batch and grain size i.e. the WC-1.3 μm to WC-4.1 μm powder batches. The laboratory milled batches (PRZ-lab and NP-lab) were made from the exact same raw materials, with the recycled material displaying better particle stability than the new powder with a zeta potential of -22.2mV compared to -4.6mV respectively. NP-prod and PRZ-prod show the same trend. The PRZ powders all possessed negative zeta potentials that were not close to zero (-16 to -25mV and -30mV in the case of the as-recycled PRZ material prior to lab milling), and AC-lab also possessed a strongly negative zeta potential. The

new powders of varying grain size showed fluctuating zeta potentials across a wide range of values from close to zero, to more negative values with no observable trend. The standard deviations of all the zeta potentials were large, ranging from 15 to 25mV, indicating that all the slurries agglomerated with time, irrespective of being subjected to recycling. The zeta potential of pure Co was measured to be positive at +7.15mV, while that of pure WC was negative at -5.21mV). Since WC-Co slurries comprise oppositely charged particles in suspension, they experience a tendency to agglomerate. The data indicates a trend that recycled materials possesses a more consistent zeta potential than new materials, but they still agglomerate and the difference is not always obvious.

The gradient of the settling rate curves (Figure 4-36, p 121) of the recycled PRZ powders displayed less variation than that of the new powders. A change in the gradient of a settling test indicates particle agglomeration and thus the rheometer reads this as a change in viscosity [79]. The gradient of the NP-lab powder from Figure 4-38 (p 124, alcohol fraction of 16.67wt %) with a gradient of 0.0127 was almost twice that of the PRZ-lab gradient which was 0.0066. The same result was seen in Figure 4-36 (p 121, 11.89wt% ethanol) and Figure 4-38 (p 124, comparing NP-prod, PRZ-prod and PRZ-prod-remill at 13.65wt% ethanol) for the higher solids loading conditions, with the zinc recycled powders showing almost horizontal settling rates in each case. It would be misleading to attribute the more horizontal settling rates of the recycled materials to better slurry stability (and correlate this with zeta potential) alone, as grain size effects and the degree of separation of the grains in the slurry, also need to be considered. From Figure 4-36 (p 121), where all the powders are compared in terms of settling rates at high solids loading, the coarser powders (possessing lower apparent viscosity) were seen to exhibit more horizontal settling rates, than the finer powders. Furthermore, NP-prod-remill and PRZ-prod possessed very similar mean volume particle sizes, of 1.93 and 1.90 μm respectively, and almost the same zeta potential. The particle size data in Table 9 (p 112) shows that PRZ-prod contained finer D10 particles and coarser D90 particles than NP-prod-remill. PRZ-prod had a lower apparent viscosity during settling and a lower rate of settling.

Particle size distribution plays a role in the packing efficiency of the particles within the slurry, and thus the flow behaviour [59, 65, 102]. Furthermore, the coarser the particles, the further the separation distance that exists between adjacent particles. Hence the attractive effect of oppositely charged grains falls off, because attractive (or repulsive) forces, in response to charge, fall off with distance, following an inverse square law. Therefore, the more separated the particles are by solvent, the less charged inter-particle interaction is possible, and the less opportunity for particle agglomeration and settling. Therefore, since all the zeta potentials fell within an agglomerating range (0 to $\sim \pm 30\text{mV}$) and the fact that settling rates were observed to be lower for the slurries containing larger particles, it is evident that, again, particle size effects were dominant over the zeta potential, and that particle size distribution, separation and distance were largely responsible for the coarser new slurries and the recycled slurries experiencing better settling rates. Furthermore, since a constant weight percent of dispersant was used, a larger particle size means less surface area for adsorption, hence more dispersant was available to attach to the particles in solution, thereby dropping the viscosity by creating a better dispersed slurry, while holding its particles in suspension. Figure 5-4 (p 170) showed the apparent viscosity at a shear rate of 500s^{-1} against mean volume grain size. The highest measured slurry viscosity was used because it more closely approximates the slurry conditions experienced during spray drying, in which shear rates of 10^4 to 10^6 s^{-1} can be experienced by the slurry as it exits the spray nozzle [54]. The data points from the recycled PRZ-lab and PRZ-prod powders appear to correspond to the trend observed with the new powders. Hence, it can be postulated that if the grain size distributions are similar or the same, and all other variables are held constant, the viscosity at high shear rates of new and recycled powders are effectively the same. This bodes well for the use of zinc recycled materials in industrial powder production.

The yield stress for all the powder batches were calculated using the Bingham plastic model of extrapolating a straight line to the y-axis, the y-intercept being the approximate yield stress of the slurry (at zero shear rate). NP-lab and PRZ-lab were spray dried at 16.67wt% ethanol while all the production powder batches

were spray dried at 13.65wt% ethanol. From Figure 4-37 (p 122), NP-lab displayed a calculable yield stress of 3.85Pa, while PRZ-lab was 1.15Pa, and AC-lab: 7.56Pa, which was by far the highest yield stress of the three lab-milled slurries, despite the high alcohol fraction of 16.67wt%. The yield stress, associated with thick slurries, results when particles are locked into rigid geometric patterns and are not dispersed [63]. A high percentage of solids loading and the extent of fine particles within the slurry are two major factors that influence the development of a yield stress value [63]. Comparing the SEM micrographs of NP-lab and PRZ-lab spray dried granules (p 103 - 104), both slurries produced hollow granules, especially noticeable in the larger granules. Therefore, neither slurry possessed a yield stress sufficient to retard the migration of the solid content within the slurry, to the surface of the granule, during droplet drying in the spray drier. The apparent density and flow rate (p 107) of NP-lab and PRZ-lab were within 0.6g/cm³ of each other, with flow rates of 18-19s, indicating no difference between the zinc recycled and new powders. The granules were not ideal because of the large internal voids. A higher yield stress is required in order to produce ideal, solid granules.

Volume percent solids is a critical parameter in slurry rheology [62]. NP-prod and NP-prod-remill both possessed yield stress values higher than 6Pa, while PRZ-prod had a yield stress of only 0.83Pa. The yield stress results correlate with the SEM analysis of the powder granules (Figure 4-26 and 4-27, p 103 - 104). PRZ-prod, AC-lab and NP-prod-remill had almost solid granules, with some internal voids, indicative of a sufficient yield stress to retard solid migration to the surface with the mobile liquid front during spray drying. Despite a yield stress of 6.91Pa, NP-prod-remill formed hollow granules, as did PRZ-prod, but AC-lab formed solid granules. Therefore, a yield stress of greater than or equal to 7Pa, was sufficient to produce granules with smaller internal voids and more solid granules, while slurries with a yield stress of less than 7Pa, resulted in hollow granules. NP-prod produced solid granules with a yield stress of 9.20Pa. Hence, to always ensure solid granules, a yield stress of around 10Pa would be ideal. Granule microstructures are known to affect the production process and properties of the

final components. Walker et al. [54] and Bertrand et al. [55] both studied the effects of slurry rheology on the properties of spray dried alumina powders. Both papers reported that the packing density of the particles (grains) within spray dried granules is lower for slurries with higher yield stress and is dependent on the slurry solids loading. The more heavily loaded the solids in a slurry, i.e. the lower the fraction of solvent present, the higher the yield stress and the less particle rearrangement is possible during the spray drying process. When the yield stress was low, both authors [54, 55] reported that a large internal crater formed, as has been observed in the spray dried powders produced in this work. The authors reported that a rigid shell is formed, in which the grains are tightly packed, to an even higher density (of the wall region) than a typical solid granule. The more highly solid loaded slurries produced a higher yield stress and more solid granules, as was demonstrated in the current research for the WC-Co system. The formation of solid granules is also related to the floc structure that exists within a slurry [54]. If the slurry is highly flocculated, it possesses a higher yield stress, consequently producing dense granules. As droplets leave the spray nozzle during spray drying, the shear rate quickly disappears and the rheological behaviour of the droplet is thereafter dominated by the yield stress [54]. If the yield stress is low, the particles readily move past one another within the drying droplet, and pack to a high density in the granule shell. Conversely, if the drag forces are high, the grains are unable to arrange as closely and do not migrate to the surface of the granule with the evaporating liquid front.

The implication of granule structure and deformation behaviour of alumina powders were studied by Eckhard and Nebelung [103] who highlighted that microstructure in combination with deformation behaviour impacts the residual defects present in pressed products and consequently, the final sintered product. Comparing hollow and solid granules, they reported that hollow granules possessed a harder shell, which was more difficult to break under pressure (because of the densely packed grains) compared to the solid granules. The dispersant level is an important factor in changing slurry yield stress and consequently granule structure [103]. In this work, the dispersant level was held

constant, hence, coarser particles (possessing lower total surface areas) can be considered better dispersed (having a higher effective concentration of dispersant, per unit surface area available) which is partly responsible for the formation of hollow granules in the case of NP-prod-remill and PRZ-prod. The dispersant is also a factor in PRZ-lab and NP-lab, but to a lesser extent, because the slurries had less solids loading when spray dried, hence, particle interaction effects between the particles were less pronounced. Coarser powders, regardless of recycling or not, produced hollow granules at the solids loading proportions studied in this work. In order to compensate for this to produce ideal granules, the alcohol fraction would need to be reduced, or the dispersant reduced, or a combination of both. The apparent density (Figure 4-29, p 107) of all of the powders spray dried in this work was between 3.4g/cm^3 and 4.0g/cm^3 . The granule size distributions were similar for each powder screen. The powders behaved similarly in terms of flow and density trends, with the largest differences existing between the granule microstructures. The powders with hollow granules (resulting from a low slurry yield stress) such as NP-lab and PRZ-lab, experienced greater fluctuations in powder density and flow rate across the range of screen fractions tested, compared to the powders with dense granules (NP-prod and AC-lab). Furthermore, it has been noted from literature that hollow granules can be expected to impact pressing behaviour and defects within the final product [103]. The results show that recycled and new slurries can both be spray dried to produce ideal granules by controlling the slurry viscosity and yield stress: requiring a balance of solid loading, charge balance (zeta potential), dispersant and particle size distribution.

5.7 Powder rheology

The purpose of powder granulation (such as spray drying) is to create free flowing, reliable powders to facilitate ease of powder handling and compaction processes. The more predictable and stable the powder flow, the higher productivity becomes during manufacturing. Powder rheology: the study of the flow behaviour of powders, therefore allows for the improvement and optimization of powder

production processes. The interpretation and production implications of the various new and recycled spray dried powders are discussed in this chapter.

The particle size distributions for each screen fraction, upon which powder rheology was performed, are shown in Table 7 (p 101). NP-prod possessed coarser particles in the 45-63 μ m screen fraction across the particle size distribution (D10, D50, D90 and Mv particle sizes) than the other powders. The particle size distributions were similar between the powders for the coarser sizes i.e. 90-125 μ m and 150-180 μ m. The results of the 45-63 μ m screen fractions in Table 7 (p 101) agree with the images shown in Figure 4-27 (p 104), where NP-prod powder possessed more consistent particle sizes with fewer fine and irregular particles in the SEM micrographs, compared to the other powders. Despite most particle sizes being similar, Figure 4-29 A and B (the apparent density and flow rate data, p 107) showed large differences in flow behaviour and density between NP-prod, AC-lab and the other powders at every screen fraction size. NP-prod consistently flowed the fastest (for the same mass of powder tested each time) compared to the others. NP-prod and AC-lab displayed the most consistent apparent densities between the screen fractions, while the other powders varied considerably. AC-lab was noticeably less dense than the other powders, despite possessing solid granules. The batch chemistry of the material was previously verified using micro-PIXE and ICP-OES, therefore the porosity is a powder property and not a metallurgical property.

The different densities and flow behaviours between the powders can be largely attributed to the granule microstructures. Comparing Figure 4-26 (the SEM micrographs of the 150-180 μ m screen fraction, p 103 with Figure 4-27 (the SEM micrographs of the 45-63 μ m screen fraction, p 104), it can be seen that the large particles possessed a higher degree of internal porosity and a higher frequency of large internal voids, compared to the smaller granules. This occurred because when a droplet is dried within a spray dryer, a smaller droplet, with its larger surface area to volume ratio, dries more quickly than a large droplet. If the slurry yield stress is low as mentioned above, the solids within the droplet are able to

move with the drying liquid front, towards the surface of the granule as it dries. A large droplet takes more time to dry than a small droplet, allowing more time for particle rearrangement to take place and therefore this longer drying time favours the formation of a shell especially if the slurry yield stress is low.

The way the individual powder granules roll and move during powder flow is clearly a major factor in the rheology of the bulk powders, hence a simple comparison model between different granule shapes has been illustrated in Figure 5-5 on the following page. The effects of 3 spherical geometries on the object's moment of inertia are shown in Figure 5-5 A-C. Figure 5-5 A represents a solid sphere, B: a spherical shell and C: a thick walled spherical object with a hollow (such as a hollow granule).

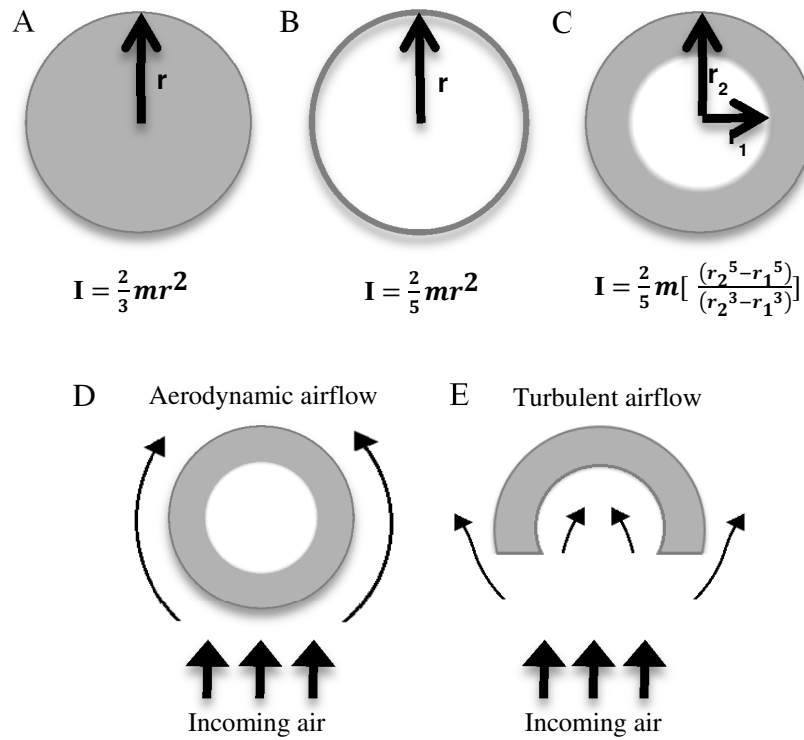


Figure 5-5 Graphical representation of the moments of inertia of spherical objects of mass ‘ m ’ and radius ‘ r ’ for A: a solid sphere, B: a spherical shell, C: a thick walled spherical shell. D: Aerodynamic airflow of a solid or closed surface sphere, representing a granule. E: Turbulent flow of a broken, thick granule, that can reduce a powder’s ability to de-aerate or flow optimally when aerated.

The formulae for moment of inertia can be easily derived. Moment of inertia expresses a body’s ability to resist angular acceleration which is determined by the sum of the products of the mass of each particle in the body, with the square of the distance from the axis of rotation. A spherical thin shell (Figure 5-5 B) of the same mass as A and C cannot happen practically in powder metallurgy and it is an idealized case, shown merely for demonstration purposes. Spherical geometries representing A and C are possible in real powders, where a thick walled shell compared to a solid granule are possible.

Walker et al. [54] proposed a model for spray dried granule formation of flocculated and deflocculated slurries which produce solid granules or hollow

granules depending on the slurry yield stress. In this model, the deflocculated (highly dispersed) slurry produced granules with a densely packed shell and an internal void, while the flocculated slurries produced solid, but less dense granules, containing a number of smaller pores [54], similar to the results found in this study. From Figure 5-5, it can be appreciated that a solid granule of mass 'm' has a lower moment of inertia relative to a granule that possesses a shell with an internal void, also of mass 'm'. Therefore, spherical powder granules with large internal voids have less ability to resist angular acceleration (a lower moment of inertia) than solid particles.

When energy is applied to the powders to initiate flow, the hollow powders expend more energy in rotational motion and less energy in translational motion i.e. motion in the direction of the applied force. Furthermore, this concept is based upon the assumption of perfect spheres, which granules are not. Figure 4-26 (p 103) indicates that the internal void and granule mass distribution are not balanced in most granules; therefore the centre of mass is not at the geometric centre of each sphere. As a result of the mass imbalance and the lower moment of inertia, powders with hollow morphologies can be expected to behave less predictably from ideal dense granules. A spheroid granule with an 'off-centre' centre of mass can be expected to require greater energy to initiate flow if the granule occupies a position in the powder bed where its centre of mass is oriented downwards for example at the so called '6 o'clock position'. The granule, therefore, possesses lower gravitational potential energy than if the granule is perched with its centre of mass at a higher point (with more potential energy), for example at a '9 o'clock or 12 o'clock' position. As such, powder with hollow granules, variable wall thicknesses and an off-centre centre of mass, can be expected to flow less predictably and less linearly in terms of flow direction than dense powders. When the dynamic analysis flow data in Figure 4-39 (p 127) is considered, it is clear that NP-prod (with its dense, round and uniform granules) consistently required less energy to flow than the other powders of the same screen fraction size. Figure 5-6 shows the normalized basic flow energy (NBFE) which takes the differences in sample mass between different powders into consideration by dividing the basic

flowability energy (BFE) by the sample mass of each powder [70]. Recall that the BFE was calculated as the flow energy of each powder at test 7, i.e. after repeated testing at 100mm/s tip speed.

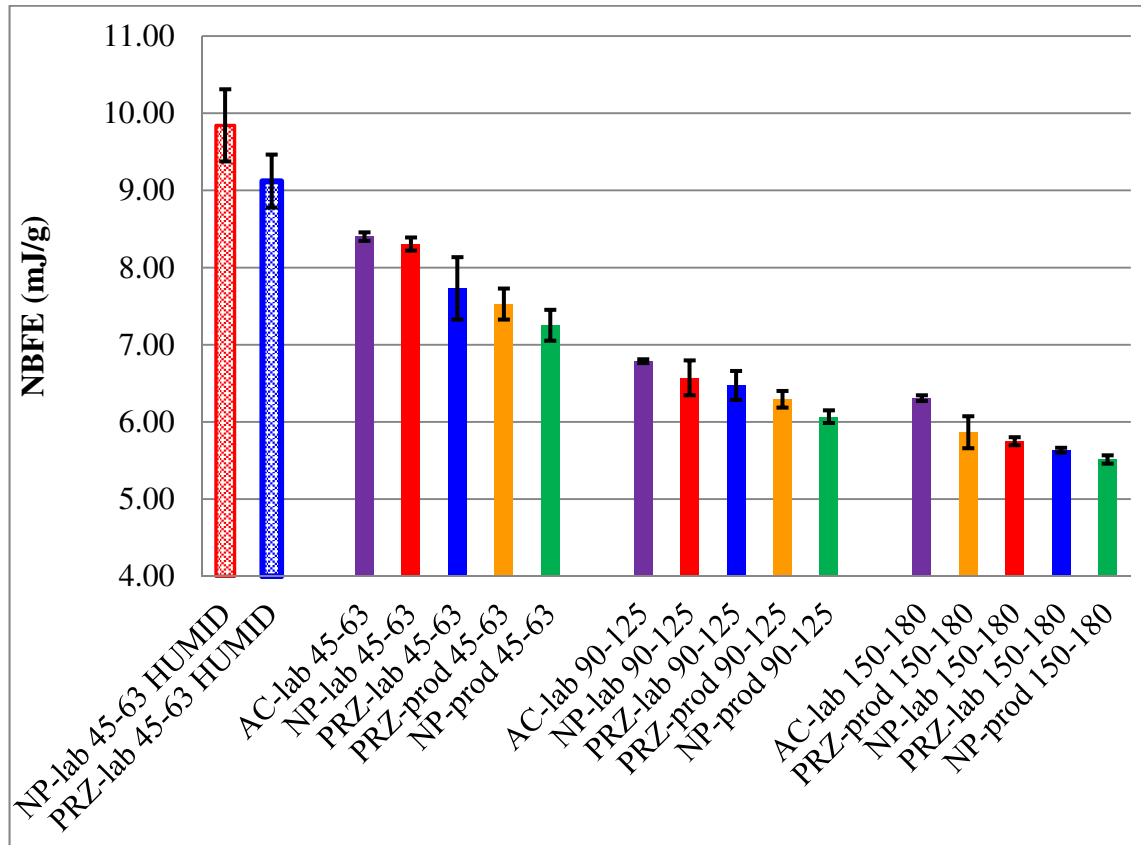


Figure 5-6 Normalized basic flowability energy (mJ/g) for each powder.

In Figure 5-6, the NBFE (mJ/g) has been plotted for each powder ranked left to right from the highest to lowest value. NP-lab humid followed by PRZ-lab humid possessed the highest NBFE. The normalized flow energies for the dry powders followed a repeating pattern from highest to lowest for the 45-63 μ m and 90-125 μ m screen fractions with AC-lab, NP-lab, PRZ-lab, PRZ-prod and then NP-prod. The coarsest screen fraction (150-180 μ m) underwent a shift in rank order because of PRZ-prod, which had larger errors and more variable flow, but nevertheless NP-prod still emerged with the lowest normalized flow energy overall, which confirms the fast flow rate results of NP-prod shown in Figure 4-29 (p 107). The dynamic analysis results (Figure 4-39, p 127) were ranked into 3

energy bands based on particle size. The widest energy band belonged to the finest particles (45-63 μ m) because with a finer powder, a larger surface area is exposed per unit mass of powder, and many more inter-particle contact points within the powder bulk, resulting in a more cohesive powder with a higher flow energy [71, 73, 104].

Differences between the powders were most pronounced in the finest screen fraction, with diminishing effect as the particles increased in coarseness. Since WC based powders are ‘heavy metal’ powders, they possess a high density even in the spray dried powder state, higher than many other pharmaceutical or ceramic powders, many of which have densities less than 1g/cc [54, 73, 75]. The effects of interparticle forces, cohesive forces and charge effects on WC powder flow are therefore difficult to detect especially at coarser particle sizes because the particles have a high mass and therefore high potential energy and momentum (if moving). When coupled with fewer contact points this overrides the effects of interparticle forces that can noticeably affect the flow of smaller particle sizes. In the reducing flow rate zone, the 90-125 μ m and 150-180 μ m sizes (band 1 and 2) on Figure 4-39 (p 127) had flow rate indices (FRI) close to 1 (also appreciated by the gentle gradient of the curve in the reducing flow rate zone), indicating that the powders were not very susceptible to an order of magnitude change in tip speed and remained highly flowable even at 10mm/s tip speed. The 45-63 μ m powders had an FRI of 1.07 to 1.13, with PRZ-prod possessing an FRI of 1.21. Hence, the finer powders experienced more difficulty flowing than their coarser counterparts with the flow results for the PRZ-prod 45-63 μ m powder agreeing with the poor flow results of the same screen fraction in the flow rate test in Figure 4-29 (p 107). PRZ-prod possessed the finest overall (Mv) particle size for the 45-63 μ m screen fraction and also a large number of visible fine and irregular or broken particles (Figure 4-27, p 104) which contributed to its poor flow rate. Figure 4-28 (p 105) also shows that this powder possessed very fine particles adhering to each granule, thus increasing the resistance and granule interlocking experienced by the powder during flow.

The humidified powder flow curves in Figure 4-39 (p 127) and the normalized energies in Figure 5-6 (p 182) illustrate that at 75% relative humidity the flowability of powders is strongly affected. The humidified powders required up to 18-19% more energy per gram to initiate flow at 100mm/s tip speed. Humidity changed the powder behaviour because 2wt% polyethylene glycol was used as a polymeric binder which facilitates pressing of the powder into a green compact. Andersson and Bergström [105] studied the friction and adhesion of spray dried cemented carbide granules containing polyethylene glycol (PEG) using atomic force microscopy. They found that granule-wall friction was controlled by the binder content and the relative humidity. The binder content, however, was held constant at 2.0wt% for each powder studied in this work and therefore did not play a role in the differences between powders, whereas in their work, they studied varying PEG combinations. An increase in the granule plasticity was found by Andersson and Bergström [105] caused by the polymer binder (PEG) becoming softer and absorbing water at increasing relative humidities. They also found that the granule-granule friction forces were lower than the granule-wall friction at all PEG contents, which they attributed to the granule-granule contact area being smaller than a granule-wall contact because of the flatness of the wall compared to the small contact points of two adjacent granules.

This work agrees with the results found by Andersson and Bergström [105] with respect to the effects of humidity on spray dried cemented carbide powders on flowability. Andersson and Bergström found that wall friction coefficient increased with increasing relative humidity; however the wall friction and angle of internal friction data in Table 11 (p 133) of this study do not show such a trend, in which we would expect the wall friction angle to increase with humidity. Rather, Table 12 (p 143) shows a decrease in wall friction was experienced by both powders. Despite a change in particle diameter by a factor of 3 the difference between the maximum and minimum wall friction angles in Table 12 was less than 4°. Since Andersson and Bergström [105] used highly sensitive atomic force microscopy measurements and the fact that only very small differences in the wall friction angle were detected on the FT4 powder rheometer, it is suggested that the

rheometer may not be sensitive enough to detect the full effects of humidity on granulated cemented carbide powders. Furthermore, the angle of internal friction, derived from the shear tests, also showed very little difference between the 45-63 μ m powders and the 150-180 μ m powders. The shear behaviour of the powders was less clearly affected by either humidity or the particle size, than the flowability, with many of the shear curves overlapping in Figure 4-40 (p 130), despite having very different particle sizes. The highest shear response was measured for the humid and fine fraction of the powders. The shear test uses a similar test routine to the wall friction test on the FT4 powder rheometer, and the shear results were unremarkable, showing differences based primarily upon particle size with unreliable differences detected from humidity measurements. For example, in Figure 4-40 (p 130) there is little difference between NP-lab humid and NP-lab (45-63 μ m powders) with possible error bar overlap, while the flowability tests (Figure 4-39, p 127) showed significant differences between these powders with no overlap between the results.

Powder compressibility results (Figure 4-41, p 132) showed very similar compressibility behaviour for all of the 90-125 μ m and the 150-180 μ m powders. Differences in compressibility were observed for the 45-63 μ m powders compared to the coarser powders, with large differences in compressibility between the humidified and dry powders. Andersson and Bergström [105] reported that cemented carbide granules softened in response to relative humidity; hence the increase in compressibility with humidity can be explained by granule softening and deformation under the applied normal stress and better powder cohesion. PRZ-prod and AC-lab 45-63 μ m powders were more compressible because of the fine, broken and irregular granules as well the adherent dust it contained (see Figure 4-28, p 105) leading to rearrangement of the powder bed under pressure and powder cohesion. Furthermore, Leturia et al. [70] observed that poorly flowing bulk solids (such as PRZ-prod 45-63 μ m) are more compressible than free flowing bulk solids, and Ahmad and Pilpel [104] observed that such powders can cause domes and arches when powder flows through an orifice, potentially causing blockages. The findings of these researchers supports the poor flow rate results

obtained for PRZ-prod and AC-lab 45-63 μ m powders, as a result of the adherent fine particles.

The powders responded similarly to aeration and fluidization testing (Figure 4-42, p 135) with three distinct flow energy bands based upon the screen fraction size. Humidity did not affect the ability to fluidize because of the heavy mass of WC powders dominating over adhesion effects, especially when air flow was introduced against gravity (from below), hence lifting the granules off each other. Bruni et al. [106, 107] found that interparticle forces due to adding small or large fine particles can change the structure of the settled bed after fluidization, and the ability of the powder to flow and achieve fluidization, and that small fines increase the resistance to flow [106]. Figure 4-42 (p 135) showed that NP-prod and PRZ-prod both required more applied air speed to reduce their flow energy, across the various air flow speeds. PRZ-prod, discussed above, possessed fine particles that adhered to the granules, while NP-prod possessed a coarser fine fraction than the other powders, hence these results agree with Bruni's analysis and NP-prod required more air speed because of its coarser, fine particles and spherical, aerodynamic nature; while PRZ-prod required more energy to overcome the adhesion caused by the adherent fines. AC-lab showed the same trend for the 150-180 μ m size fraction at lower air velocities (< 20mm/s), but fluidized well despite some adherent fine particles, at the smaller screen fraction sizes. Hence, although trends are observable with NP-prod and PRZ-prod, AC-lab did not behave in exactly the same way despite solid granules and some adherent fines, illustrating the complexity of powder flow. It is suggested that a multitude of factors come into play, such as the powder density, granule structure and inertial properties, adherent fines, granule size distribution, granule surface properties etc.

None of the powders retained air after the second de-aeration cycle in the de-aeration tests (Figure 4-43, p 137), however the humidified powders experienced the greatest changes in flow energy after aeration, indicating that they retained more air. The results indicated that powder aeration can improve the flowability of humidified powders temporarily. In permeability tests (Figure 4-44, p 138) the

humid powders underwent a high pressure drop, because of increased powder compressibility at each applied normal stress, hence creating a tortuous path for air to traverse the powder bed.

NP-prod possessed lower flow energy than the other powders in the 45-63 μ m and 90-125 μ m screen fractions in the de-aeration testing (Figure 4-43, p 137) and again emerged with the best overall permeability results (lowest pressure drop across the powder bed) compared to the other dry powders. Solid dense granules can de-aerate efficiently and hence punch speeds and production rates could be increased with highly permeable powder in manufacturing because it allows the air to escape rapidly rather than creating an airlock or pressure gradient. AC-lab perhaps did not de-aerate to the same degree as NP-prod, because it's broad slurry grain size distribution affected the spray dried apparent density of the powder bulk, this means that each granule is less dense i.e. more porous, than the NP-prod counterparts. A more porous powder (in terms of intra-granular porosity) could retain air and therefore de-aerate to a lesser extent and also fluidize more easily, as each pore could act as an air pocket, increasing aerodynamic drag.

Freeman [75] stated that the presence or absence of air is arguably the most important of the many factors affecting powder flow properties. In this work, the solid, dense granules displayed the best behaviour in terms of aeration testing, and a reason for this is suggested in Figure 5-5 D and E (p 180). A solid granule or a granule that is externally spherical but contains an internal void (Figure 5-5 D), is more aerodynamic than a broken granule (Figure 5-5 E) which would cause turbulent flow in an airstream. Also, a broken granule could act as a 'parachute' or 'air trap', preventing the air from escaping the powder bed easily. The same is true of granules that are porous, such as AC-lab, due to poor packing of differently sized particles. Irregular granules (which can interlock) and those with an 'off-centre' centre of mass can also be expected to be less predictable in terms of aerated flow (or fluidization) and de-aeration than ideal, dense, spherical granule. In the case of zinc recycled powders compared to new powders, the recycling history of the powders did not directly impact the powder rheology as proven by the fact that

NP-lab (100% new powder) and PRZ-lab (100% zinc recycled powder) behaved similarly in all rheological testing. Rather, spray dried granule microstructure and particle size distributions that resulted from the slurries of the zinc recycled and new powders directly controlled the powder rheology, as did the humidity of the environment the powders were exposed to. By controlling the slurry rheology of the precursor slurries carefully, both zinc recycled and new WC powders can be produced with the same rheological behaviour.

5.8 Compaction behaviour

The zinc recycled and new powders pressed similarly across the shrinkage range of 17 to 22%, indicating that both are equally suitable for component manufacturing. They displayed a tendency to crack when pressed at low and high shrinkages (17% and 22% respectively), below and above the ideal shrinkage range of approximately 20% for such powders. At 22% shrinkage, the powders were insufficiently compacted, hence exhibiting low green strength and consequently cracking, and were ‘over-pressed’ at 17% shrinkage. This phenomenon has been frequently observed at Pilot Tools.

The AC-lab powder did not crack at 17% shrinkage or 26% shrinkage. The fine grain size fraction within the AC-lab powder, combined with the coarse fraction, potentially allowed for greater particle rearrangement and interlocking under high pressure compaction. King [108] reported that shrinkage directly depends on grain size, with fine grain sizes experiencing large shrinkages and coarse grain sizes require lower shrinkages in compaction processes, it is therefore suggested that a combination of the two grain sizes in the AC-lab powder increased the shrinkage tolerance of this powder. Sánchez et al. [109] found that the green strength of iron powder compacts increased as particle size decreased, but flowability and compressibility decreased with decreasing grain size. Hence, the reason for the higher pressing force trend of AC-lab is the larger surface area of the fine particles - requiring a larger applied force to achieve the required dimensions for the

pressed cylinder. The finer particles also contributed to improving green strength, preventing cracking, as was noted by Sánchez et al. [109]. This is consistent with the slurry rheology results, in which a higher shear stress was recorded compared to NP-lab and PRZ-lab, because of the large surface area imparted by the fine particles within the material. No such trend was observed in the powder rheology compaction results, because the force was too low to cause granule breakdown and grain rearrangement. Rather, the powder rheology compaction test merely indicates granule rearrangement under low pressures.

5.9 Sintered material properties

This section discusses the sintered material properties of the new and recycled materials and their significance to the cemented carbide manufacturing process.

The NP materials were within the benchmark metallurgical specifications (Table 13, p 147), but with a slightly higher than ideal coercivity, due to the fine grain size resulting from over-milling. As discussed earlier, the new powders mill more quickly than the recycled powders, with a finer (narrower) overall slurry particle size distribution. The dependence of magnetic coercivity on grain size and its use in quality control is a well-documented phenomenon in cemented carbides [10, 30, 32].

The SEM micrographs at 5000X and 10000X (Figures 4-48 and 4-49, p 144 - 145) of the sintered microstructures of the WC-6wt% Co alloys, showed that the finest sintered grain size distribution belonged to the NP materials. In sintering of cemented carbides, Ostwald ripening occurs in which the large, undissolved grains grow by re-precipitation of WC, at the expense of the smaller grains [24]. Since the new powders possessed such a narrow slurry particle grain size distribution, the final sintered grain size was consequently smaller. The PRZ alloy properties were within all the benchmark ranges, and had a coarser microstructure than the NP alloy, but finer than the AC alloy, with a few isolated large WC

grains. The AC alloy properties did not meet most of the benchmark values; an unacceptably high magnetic saturation value, a low coercivity and Vickers hardness, but an acceptable density. It also possessed some unusually coarse grains.

The magnetic saturation of the AC alloy was high due to iron contamination, originating from the repeated milling cycles (in stainless steel mills) to which the powder was exposed. During its material lifespan the first series of milling cycles arose during production of the new alloy (before recycling), then the scrapped tool was subjected to the zinc recycling process which included crushing and milling to break down the recycled product, from which the oversize material was extracted and subjected to acid leaching, after which this recycled product was milled to down to the required production grain size, and further homogenized with the addition of extra cobalt powder to achieve the required composition. The addition of the extra cobalt depended upon accuracy of the ICP-OES data. For example, an 'under-reading' by ICP-OES of the cobalt content of the acetic acid recycled material by 0.1 to 0.2wt% Co, could cause a detectable increase in magnetic saturation due to a small excess of cobalt within the final material, added during milling in order to balance the batch according to the ICP result. Hence, when producing recycled materials and measuring the composition of the recycled feedstock, it is preferable to attain the most accurate chemical composition possible to reduce errors, otherwise, a batch may need to be reprocessed to correct its chemical composition.

The coercivity was low for two reasons, namely the presence of too much magnetic material (i.e. predominantly Co with Fe contamination), and the coarse sintered grain size of the alloy. The large number of very fine ($< 0.5\mu\text{m}$) grains in the green compact, which have a large surface area and a tendency to react and dissolve, were consumed by the coarser grains during liquid phase sintering, as per Ostwald ripening [24]. This process resulted in the coarse grained microstructure depicted in Figure 4-48 (p 144) and 4-49 (p 145) which is directly responsible for the low Vickers hardness. The AC alloy had an acceptable density

with no visible porosity, which is attributed to the predominantly solid powder granules produced from the slurries.

Based on the sintered material properties, the PRZ powders are suitable to be used for the production of the specified mining grade tools, but the AC powders are unsuitable for this specific mining tool application. However, based on the sintered properties, the AC powders may be used for alternative applications, e.g. components which require high fracture toughness, where the coarser grained hardmetals are generally used. Benchmark ranges for existing hardmetal grades include a Vickers hardness of 1150-1290 HV30 and a coercivity of 80-120Oe. The composition of the AC powders could be adjusted as necessary to increase the cobalt content, to produce even tougher grades which are suitable for applications such as milling media, shims, and possibly coal and hard rock mining [110].

5.10 Financial analysis and industrial viability

This section discusses a simple cost comparison of the zinc recycling and acetic acid recycling processes, as well as providing advantages and disadvantages of each method.

The acetic acid process is slow to leach fully dense, sintered cemented carbide parts [3], hence the reason it was investigated as a supplementary process to the zinc recycling process in this work, and not a full replacement. Nevertheless, the comparison of the two, full-scale processes is demonstrated in this section for ease of comparison, and is discussed in detail. A cost comparison was performed of the basic setup costs of both plant types, as well as the operational costs. The cost analysis is not exhaustive, but it incorporates data accumulated during the course of this work as well as costs observed during commercial production at Pilot Tools.

The initial costs of a PRZ plant are estimated at approximately 4 million South African Rands [111], which includes the costs of the furnace, elements, dry mill, powder crusher, vacuum distillation pump and attachments. The said PRZ plant can accommodate 1100kg of WC scrap per cycle, and takes less than 1 week to complete an entire cycle. The setup cost of a 100kg acetic acid plant (manufactured in this study, as outlined in the methodology) was R28 000. Both plants require initial costs of materials such as zinc ingots and acetic and oxalic acids etc, which haven't been included in the initial setup calculation (based on equipment only).

In order to compare the acetic acid method consistently with the PRZ process, a basic cost per kilogram and time for manufacture needs to be considered. A single PRZ plant at Pilot Tools consistency consumes 4400kg of cemented carbide scrap per month, achieving at least a 90% yield on the first furnace run (the other 10% or less results in dense or porous oversize material). Therefore, in order to compare within the same time scale of monthly output, the acetic acid plant would need to also accept 4400kg of scrap each month. Hence, 44 acetic acid tanks built in the same way as outlined in this work, would cost over R1.2 million to set up, cheaper than the PRZ setup cost.

The running costs of the zinc recycling plant are shown in Table 14 (next page), and those of the 'scaled-up equivalent' acetic acid plant appear in Table 15 (p 194). The overall cost and efficiency comparison appears in Table 16 (p 195).

Table 14: Running costs of a zinc based cemented carbide recycling plant in South African Rands.

Description	Unit	Unit Price	Used Per Month	Final Price	Comment
Scrap (Feedstock)	Cost per kg	R 280.00	4 400	R 1 232 000.00	Fixed cost (not included in running cost)
Production Target of 4400kg per month					
Zinc	Per disc	R 4 400.00	24	R 105 600.00	
Metalcote	Per 20kg	R 451.11	2	R 902.22	Non-stick Coating for graphite crucibles
O-ring	Per meter	R 59.07	10	R 590.70	Seals
Oil	Per 20ltr	R 639.80	1	R 639.80	Pump maintenance
Filters	Each	R 106.00	4	R 424.00	Pump maintenance
Water bill	Per month	R 1 202.70	1	R 1 202.70	
Electricity bill	Per month	R 58 136.58	1	R 58 136.58	
Labour (blue collar)	Per month	R 7 200.00	1	R 7 200.00	
Labour (skilled)	Days per month	R 1 710.00	4	R 6 840.00	Engineering oversight & maintenance * 2 engineers / technicians are required
50% return on zinc recycling	Per disc	-R 2 200.00	24	R -52 800.00	Recycled zinc ingots from zinc supplier that are sold at 50% initial cost
				R 128 736.00	Total excludes raw material

Table 15: Running costs of an acetic acid cemented carbide recycling plant in South African Rands.

Description	Unit	Unit Price	Used Per Month	Final price	Comment
Scrap (Feedstock)	Cost per kg	R 280.00	4 400	R 1 232 000.00	Fixed cost (not included in running cost)
Production Target of 4400kg per month					
Acetic acid	Cost per kg	R 9.00	1 100	R 9 900.00	
Electricity	R0.5 per kwh	R 0.50	95 040	R 47 520.00	
Water	R25.63 per kilolitre	R 25.63	220	R 5 638.60	
Oxalic acid	Per kg	R 10.80	565	R 6 104.16	2.14kg used to extract 1 kg of Co as CoOx
Basic labourer	Per month	R 7 200.00	2	R 14 400.00	
PPE per month	Per month	R 500.00	2	R 1 000.00	
Cobalt oxalate (CoOx) resale	Per kg	-R 18.00	829	R -14 925.60	Sum of oxalic acid + extracted Co
80% return on recovery of acetic acid	Per disc	-R 9.00	880	R -7 920.00	Regenerated by formation of CoOx
				R 61 717.16	Total excludes raw material

Table 16: Overall cost and efficiency comparison of the PRZ process and the acetic acid process.

	Running costs	Yield Achieved	Total load	Useful output	By-product amount	Unit cost	By-product cost	Final cost	Final unit cost
	(monthly)	(%)	(kg)	(kg)	(kg)	(per kg, 1st run)	(reprocessing)	(monthly)	(per kg)
	(from Table 14/15)								
PRZ	R 128 736.00	90%	4400	3960	440	R 32.51	R 28 608.00	R 157 344.00	R 39.73
Case 1		95%	4400	4180	220	R 30.80	R 13 551.16	R 142 287.16	R 34.04
Acetic	R 61 717.16	60%	4400	2640	1760	R 23.38	R 82 289.55	R 144 006.71	R 54.55
*Case 1		70%	4400	3080	1320	R 20.04	R 52 900.42	R 114 617.58	R 37.21
*Case 2		80%	4400	3520	880	R 17.53	R 30 858.58	R 92 575.74	R 26.30
*Case 3		90%	4400	3960	440	R 15.59	R 13 714.92	R 75 432.08	R 19.05

* Hypothetical scenarios at higher efficiencies (yield).

The assumptions and limitations that were used to generate the cost comparisons were:

- The cost of the scrap material was set at R280 per kg (as for August 2015), requiring 4400kg of material each month to satisfy required production outputs from a single plant (a target required by company management)
- Costs were determined at the time of assessment and are subject to change
- The recycling of zinc ingots or cobalt ‘in-house’ was beyond the scope of this project
- The acetic acid plant can regenerate 80% of the acetic acid by cobalt oxalate formation from the addition of oxalic acid
- By-product or ‘oversize’ materials are fully recycled after 2 recycling runs
- Fully dense material was not used in the acetic acid plant, as it has been investigated as a supplement to the PRZ process.

Although the running costs of the acetic acid plant (Table 15) compared to the PRZ plant (Table 14) were lower, the yield of the plant was only 60%, compared to the PRZ plant that has been known to achieve a yield of 95% if a small (< 10mm diameter) scrap size is used, or a longer run performed on larger scrap sizes. Table 16 shows the overall cost comparison of the two plants, accounting for the level of efficiency (column 3). At 95% efficiency, the PRZ plant generated useable powder at a cost of R34.04 per kg (this does not include the initial cost of the scrap, at R280 per kg). The acetic acid plant produced material at R54.55 per kg when only 60% efficient. It is important to note that this was the case even when using ‘oversize material’ from the PRZ plant. Hence, under these circumstances, it is more cost effective to simply recycle the material a second time through the PRZ plant.

As the efficiency of the acetic acid plant is theoretically increased (Table 16 column 3) the cost per kg of the acetic acid plant drops to R19.05 per kg if the plant were to be 90% efficient. Edtmaier and Meissl [3, 7] observed that the use of pressure and pure oxygen, rapidly increased the rate of cobalt dissolution. Hence, at increased initial setup cost, the efficiency could be improved by either bubbling

oxygen gas through the acetic acid or rather building pressure vessels, thereby potentially increasing the startup and operational costs. It is important to consider that the zinc recycled by-product materials already incurred the cost of the initial zinc recycling run, therefore if the acetic acid process is run at low efficiency (without pure oxygen or under pressure) and including dense oversize / by-product material, then the combination of the long running time and the high cost, is not industrially sensible. However, if the use of oxygen or pressure is added, the process becomes more efficient.

The PRZ process has a high recovery rate, produces powders with low impurity levels, and is an overall environmentally friendly process because it does not produce pollution other than through the use of electricity. The Zn may be reused for multiple recycling runs, before requiring replacement. However, its disadvantages include high peak electricity consumption, the material chemistry and composition can change through multiple recycling runs, and the material to be recycled does not always break down into powder in the first recycling run [4, 5]. The latter was observed in the current study where coarse, oversize particles were produced from partial Zn infiltration. This would require a second (or even third) recycling run to reduce it to useable feedstock for manufacturing, thereby increasing power consumption and production costs. Despite the negative aspects, it is a widely used technique. From their work, Karumaa and Kurkela [5] have predicted that the zinc recycling process will gain market share in the future as they believe that its full potential has not yet been realized.

The advantages of the acetic acid leaching process is that it can be conducted at low temperatures and pressures, and selectively leaches out the cobalt binder from between the tungsten carbide grains. A further advantage is that the acetic acid recycling process can regenerate the acetic acid by reclaiming the cobalt using oxalic acid addition, to produce cobalt oxalates (that can be converted back into cobalt) and leave the acetic acid behind. One of the main disadvantages of the leaching process used in the current study was the time period (21 days) required to produce the recycled product. If only porous oversize material was used, this

could potentially be reduced to 10 to 14 days, however. If the leaching time for the acetic acid method takes more than two weeks, the cost of 'holding' expensive stock in the process also comes into play, for example, the loss of interest in holding R1 million worth of stock for a month, instead of converting it into useable powder in less than a week. A further disadvantage (if one wishes to increase the yield) would be the need to sort the porous oversize material from the dense oversize material, and the maintenance of a second recycling method, requiring more expertise and resources. The acetic acid method poses the risk of cobalt and organic acid pollution (both are extremely toxic to waterborne life forms) being introduced into the environment, hence a purification / washing tank would be necessary if it were to be used on a larger scale - which was not taken into account in the setup costs. Based on the current study, the main advantage in employing the current acetic acid leaching process is that it can be used in combination with the PRZ process, where its primary function would be to recycle the porous oversize by-product of the PRZ process, especially if the PRZ plant is in constant use, and the company requires a monthly 'top-up' of material that would otherwise not be accommodated without a second PRZ furnace.

6. CONCLUSIONS

This thesis investigated the production implications and industrial viability of the zinc and acetic acid recycling methods to recycle cemented tungsten carbides. The research has shown that the two recycling methods may be used as complementary processes. The main research findings are highlighted in the sections below.

The distribution and concentration of major elements and impurities at various stages of the cemented carbide manufacturing and recycling processes were studied. All the grades showed high purity levels of at least 99%. The major impurity element found in all the grades was iron, which was concentrated in the Co binder phase in all the grades. A comparison of the analytical techniques used for the impurity detection showed that ICP-OES and micro-PIXE are accurate techniques for the detection of low impurity levels in hardmetals, conversely EDS was not as accurate. Micro-PIXE exhibited superior beam depth penetration and ppm levels of accuracy, compared to SEM. Zinc recycled cemented carbides had the most homogeneous Co binder distribution, followed by acetic acid recycled material. New materials had the least homogeneous Co distribution.

The formation of oversize material within the zinc recycling process was investigated. Dense oversize material was found to contain cobalt enriched, lamellar surface structures with higher zinc impurity levels than are commercially acceptable, therefore requiring a second recycling process. The porous oversize material, possessed some residual cobalt clusters but was predominantly porous. Correct sizing of the material prior to the zinc recycling process, with correct process optimization is recommended to minimize oversize material and prevent zinc retention. A prototype acetic acid plant was constructed and was used to recycle a batch of oversize material from a zinc recycling run. The porous oversize material was quickly leached and reduced while the dense oversize material leached very slowly. On the basis of the results, this acetic acid leaching process is deemed a suitable method to recycle the oversize material, instead of

subjecting the oversize to a second zinc recycling run, which would increase production costs.

The slurry rheology of new, zinc recycled and acetic acid recycled WC-6wt% Co materials were studied. The molecular weight of the PEG based binder system was unaffected by the longer milling times of the recycled materials. Grain size distribution was the dominant determining factor in slurry rheology. Shear and yield stress increased with decreasing slurry grain size, and vice versa. Slurries of low viscosity and low yield stress resulted in hollow granules when spray dried. Conversely, solid granules resulted from slurries possessing a higher viscosity and yield stress, irrespective of whether the material was new or recycled. Recycled slurries tended to exhibit consistently negative zeta potentials while new slurries displayed fluctuations in zeta potentials, averaging closer to zero. The zeta potential results were in agreement with the settling test results. Recycled slurries displayed a tendency to settle less quickly than new slurries. The slurries with the finest particle size distributions (whether new or recycled) displayed the greatest fluctuations in settling rates. The acetic acid recycling method resulted in a mixture of extremely fine and very coarse particles within the slurry. The fine particles increased the slurry yield stress beyond the other laboratory milled powders, producing solid spray dried granules despite the use of a high alcohol weight percentage. Fine particulates increased slurry yield stresses and shear responses exponentially with a decrease in particle diameter.

New and recycled powders can both be tailored to produce ideal, dense spray dried powder granules, by tailoring the properties of the precursor slurry, which was dominant in determining the final powder particle size distribution and the internal granule microstructure. All of the powders produced in this work were highly flowable. Powder rheology studies could detect flow differences between the powders. Shear tests and wall friction tests were incapable of clearly characterizing the spray dried powders, distinguishing only small differences according to particle size. Powder containing fewer fines and a coarser fine fraction, dense, spherical granules with an occasional, small internal void displayed the most consistent flowability. A very wide particle size distribution, such as that of the acetic acid produced slurry, resulted in powder granulate

of a lower bulk density due to many small voids present within the granule but with consistent flow behaviour. Powders possessing large internal voids resulted in large variations in flow behaviour and apparent density compared to dense granules. Powders with dense granules were more difficult to fluidize than hollow granules. If present, very fine particles within the powder reduced overall flowability. Powder flow energies could be ranked according to particle size distribution, with the fine powders requiring the most energy to initiate flow, and the coarse particles requiring the least. Spray dried powders exposed to 75% relative humidity experienced poor flowability, were more compressible because of PEG hydration, de-aerated less easily, were less permeable, experienced higher flow energies and experienced poor flowability under low flow rate conditions, compared to their dry counterparts. Recycled and new powders behave the same way rheologically if their granule microstructures and particle size distributions are the same and could all be readily pressed into green compacts. The broad grain size distribution of the acetic acid material led to fewer cracks across a broad range of tool shrinkages.

The zinc recycling process produced sintered alloys having properties that readily fell within the commercial benchmark ranges for WC-6wt% Co mining grade tools. Although the acetic acid recycled sintered were deemed unsuitable to manufacture the same grade of mining tools, the process cannot be viewed as a failure, since the recycled powders are still suitable for different commercial applications. The zinc recycling method does not produce environmental pollution other than through power usage, whereas the acetic acid process would require careful monitoring of spillages and chemicals, but has the advantage of regeneration of the acetic acid. The zinc process is quick and efficient, reliably producing a large production output on a regular basis. The acetic acid method is unsuitable as a complete replacement for the zinc recycling process, but could be used to supplement the zinc process successfully.

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110. Morrison, J. 2015: South Africa.
111. Morrison, N. 2015: South Africa.

8. APPENDIX

Research outputs from this work are listed here.

A. The following ISI journal papers have been published during the course of this research:

1. Freemantle, C.S. and N. Sacks, **Recycling of cemented tungsten carbide mining scrap metal**. The Journal of the South African Institute of Mining and Metallurgy, 2015. 115: pp. 1207-1213.
2. Freemantle, C.S., N. Sacks, M. Topic and C. Pineda-Vargas. **PIXE characterization of by-products resulting from the zinc recycling of industrial cemented carbides**. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2015. 363: pp. 167-172.
3. Freemantle, C.S. and N. Sacks. **The impact of zinc recycling on the slurry rheology of WC-6wt.% Co cemented carbides**. International Journal of Refractory Metals and Hard Materials, 2015. 49: pp. 99-109.
4. Freemantle, C.S., N. Sacks, M. Topic and C. Pineda-Vargas. **Impurity characterization of zinc-recycled WC-6wt.% Co cemented carbides**. International Journal of Refractory Metals and Hard Materials, 2014. 44: pp. 94-102.
5. Freemantle, C.S., N. Sacks, M. Topic and C. Pineda-Vargas. **PIXE as a characterization technique in the cutting tool industry**. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2014. 318, Part A: pp. 168-172

B. Journal papers in-progress (at the time of the thesis submission):

6. Freemantle, C.S. and N. Sacks, The characterization and rheology of new and zinc recycled WC-6wt% Co powders. Submitted to Powder Technology.

C. Conference proceedings and publications:

7. Freemantle, C.S., N. Sacks, M. Topic and C. Pineda-Vargas. **PIXE characterization of by-products resulting from the zinc recycling of industrial cemented carbides**, 14th International Conference on Particle Induced X-ray Emission, 25 February - 3 March 2015, Cape Town, South Africa.
8. Freemantle, C.S. and N. Sacks, **Particle characterization, rheology and pressing behaviour of zinc recycled and un-recycled WC-6wt.%Co powders**. Proceedings of the 9th Tungsten, Refractory and Hardmaterials Conference, Orlando, USA, ISBN 978-0-9853397-7-7, 2014. Part 1: pp 56-64.
9. Freemantle, C.S., N. Sacks, M. Topic and C. Pineda-Vargas. **PIXE as a characterization technique in the cutting tool industry**, 13th International Conference on Particle Induced X-ray Emission, 3-8 March 2013, Gramado, Brazil.