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Effect Of Process Parameters On Particle Size Distribution Characteristics Of Tungsten Powders Reduced By Powder Metallurgy Route

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ABSTRACT: The control of particle size distribution of tungsten powders is one of the key strategies in improving the performance of tungsten carbide powders for cutting tool applications. For example, grain coarsening of WC powders depends primarily on the prior grain size of tungsten powders during carburization. In this present work, effect of process parameters on reduction mechanism (Chemical vapour transport) of tungsten oxide to metallic tungsten has been extensively investigated, so as to control the uneven grain growth as well as to reduce the distribution span of the particle size to obtain the homogenized microstructure in the final sintered product. Various processing parameters such as powder layer thickness, hydrogen gas flow rate, powder feed rate and temperature have been modified in the trail experiments. Microstructural analysis was performed based on particle size distribution (PSD) and the average grain size of the reduced tungsten powders. These experimental findings can be implemented for cost effective feasible solution in high volume production unit of powder metallurgical industries.

KEYWORDS: Tungsten oxide, Tungsten, Chemical Vapour Transport, Carburization, Particle size distribution (PSD), Grain size

1. INTRODUCTION

Cemented carbide is an important class of hard and toughest composite material used extensively for cutting tool and other industrial applications. Basically, it comprised of fine particles of cemented carbide phase bonded by a ductile metal such as Co and Ni as shown in Figure 1. The most common cemented carbides include tungsten carbide (WC), titanium carbide (TiC), or tantalum carbide (TaC). The significant advantage of these carbide cutters produces a better surface finish on the machined part, and faster machining speed when compared to high-speed steel or other tool die steels. In addition, these carbide tools can withstand higher frictional temperatures encountered at the cutter-workpiece interface during machining operations. The stiffness of tungsten carbide is twice as that of steel, with a Young's modulus of approximately 500-700 GPa and its hardness is comparable with corundum (α- Al2O3). From microstructural point of view, hardness and life time of WC cutting tool can be determined by the prior grain size of the metallic tungsten powder. In powder metallurgical industry, production unit mainly focusses on controlling the average particle size of metallic tungsten powder for the subsequent carbide formation.

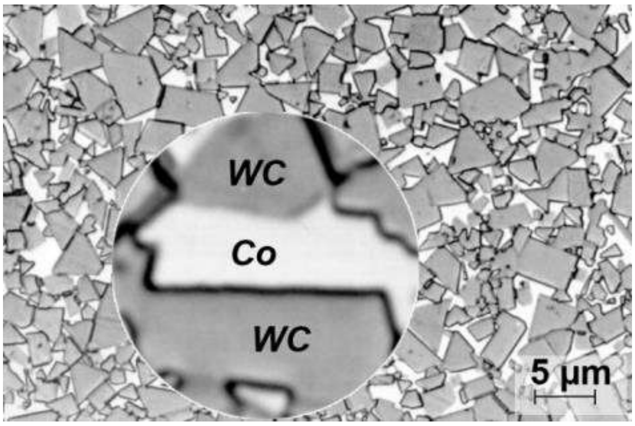


Fig 1.1. Microstructure of Tungsten carbide

The operational performance of WC cutting tool depends on three fundamental parameters namely (i) the mean WC grain size (α phase), (ii) the binder metal content (β phase) and the content of other alloy compounds (γ phase). The grain size of alpha phase WC varies from point to point in the cutting tool. It is well-known fact that the hardness or yield strength is inversely proportional to the grain size based on the Hall-Petch model given by the following equation;

$$\sigma_{yp} = \sigma_o + KD^{-1/2}$$

where σ_{yp} *and* σ_o refers to the yield strength of polycrystalline and single crystal material, K is the Hall-Petch coefficient, and D is the average grian size

The above equation suggests the fact that the hardness is very high in smaller grain region and lower in larger grain region. In cutting tool, the tool tip / nose radius is the critical parameter where the desired hardness is required. If there is a wide spread of the grain size in the microstructure then it would be difficult to control the hardness and tool life of the carbide cutting tool. Therefore, by having uniform grain size in the microstructure of the sintered product, it is feasible to obtain uniform hardness throughout the material and better tool performance. The final sintered product grain size is dependent on the Tungsten carbide particle size and in turn the WC grain size is dependent on the prior grain size of metallic tungsten powder which is influenced by the reduction conditions during WO_3 to W. Therefore, the main objective of this present work is to predict the favourable processing parameters that brings the narrow range of particle size when tungsten oxide powders are reduced to metallic tungsten. The reduction of tungsten oxide to tungsten takes place by two methods namely (i) solid state diffusion and (ii) chemical vapor transport which are briefly discussed as follows

The role of hydrogen flow rate in the reduction of tungsten oxide to tungsten powder is well established. In production unit, the most acceptable FSSS value of the metallic tungsten powder falls between 0.5 and 15 pm. The most influencing processing parameters during reduction reaction are temperature, time, hydrogen flow rate, height of oxide powder mass and apparent density of the oxide. Numerous literatures are available on reduction of tungsten oxide powders at low temperatures and the corresponding powder morphological changes and found that in production of tungsten metal, the following transition steps occur under technical reduction conditions:

WO_3 □$WO_{2.9}$ □$WO_{2.72}$ □WO_2 □W
These transition steps are characterized by colour changes (greenish blue □ dark blue □ deep violet □ brown □ grey)) in addition to complete changes in crystal morphology. The monomeric tungstic oxide hydrate, WO2 (OH)2, which always forms when tungstic oxide comes in contact with moisture at elevated temperatures, is a highly volatile compound. It has been reported on the basis of thermodynamics consideration, that the various intermediate transformation steps occurring during the reduction of WO2.9 to tungsten must be by chemical vapour transport (CVT), and the species responsible for tungsten transport in the gas phase is in all cases WO2(OH)2 (g) [1].

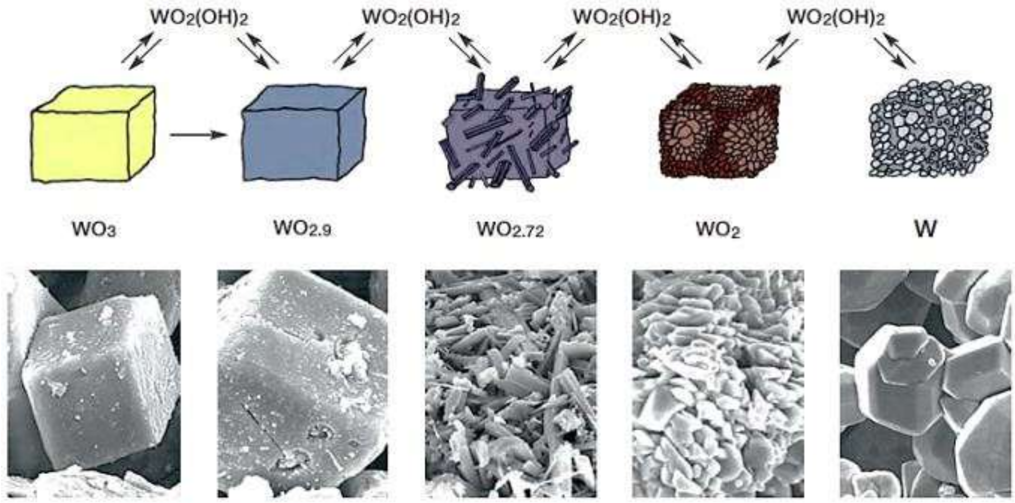


Fig 1.2. Morphological changes occur during H2 reduction of W Blue oxide

2. EXPERIMENTAL PROCEDURE

The key objective of the experimental work is to achieve at least 20% reduction of distribution span in lower grain size grade W/WC particle size distribution compared to the current level by the study of kinetics of the tungsten oxide reduction parameters resulting uneven grain growth of metallic tungsten. The process parameters which need to be optimized during the reduction of tungsten oxide to metallic tungsten powder is discussed in the following;

1.1 Working Of Reduction Furnace

There are two reduction furnaces in Kennametal Production unit. The reduction furnace is a kind of Pusher type tube furnace with 6 or 4 tubes in each. Below are the influential parameters affecting average grain size as well as for the wide span of PSD.

1.2 Powder Layer Thickness

The tungsten oxide of YTO (Yellow Tungsten Oxide / Blue Tungsten oxide is filled in the rectangular boat through programmed PLC hopper which fills powder based on the predefined weight during input program, in which weight varies for every grade to modify the powder bed thickness which in turn affects the metallic tungsten particle size.

1.3 Hydrogen Flow Control

In every tube the hydrogen will be passed in the counter flow direction to the movement of the boats at a prescribed limit. The hydrogen passed will be having the moisture content which is measured by the critical parameter of dew point, which determines the ratio of the partial pressure between H2O and H2. The higher the moisture content higher the grain growth and vice versa. The hydrogen is regenerated and recirculated to the furnace from the generated vapour during the reaction.

1.4 Temperature Control

The furnace is divided into five heating zone, where the heating coils are placed in every heating zone and the temperature in the heating zone varied from 700 to 950ºC. Based on the input power supply the resistance developed in the coils which in turns gets heated up and then heats the tube. The heating coils are placed below the tube with air gap so that the tube gets heated up due to convection and radiation heating. The coils are placed perpendicular to the direction of the tube. The temperature setting is done in PLC for particular grade.

3. FEED RATE

The feed rate of the powder loading and unloading is manual process, where the control is through alarm indication and waiting of empty boats for next set of loading. The cycle time for each boat loading and unloading in a tube is usually 15 to 20 mins based on the grade required. The operator for every 15 mins / 20 mins loads a set of WO3 filled 6 boats in 6 tubes and takes the output of 6 boats of reduced metallic Tungsten from 6 tubes. This is a continuous process and goes on throughout the shifts. It takes around six to seven hours for a particular boat to pass through the complete reduction cycle of the furnace.

The moisture content of the hydrogen is raised either by feeding hydrogen of higher humidity to the furnace or by increasing the oxide bed height to maintain a higher water vapour concentration within the layer, a remarkable increase in particle size can be achieved. The existence of a very thin layers of powder bed always produces a high temperature gradient because the moisture content can be easily removed. This results in the formation of fine-grained tungsten powder owing to high nucleation rate. However, with greater height or bed thickness, H_2O removal from the interior of the layer found to be slower and therefore the reactions conditions are close to ideal, leading to small differences in the H2O concentration, which eventually leading to large particle size aided by lower nucleation rate. The layer porosity is inversely proportional to the water vapour concentration and average particle size.

Parameters Increases during reduction	Average Particle Size
Boat Speed	Decreases
Bed Thickness	Increases
Temperature	Increases
H2 Moisture content	Increases
H2 Flow	Decreases
Layer Porosity	Decreases

Table 2.1. Parameters affecting average particle size

Laser diffraction is a widely used particle sizing technique for materials ranging from hundreds of nanometres up to several millimetres in size. Laser diffraction measures particle size distributions by measuring the angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample.

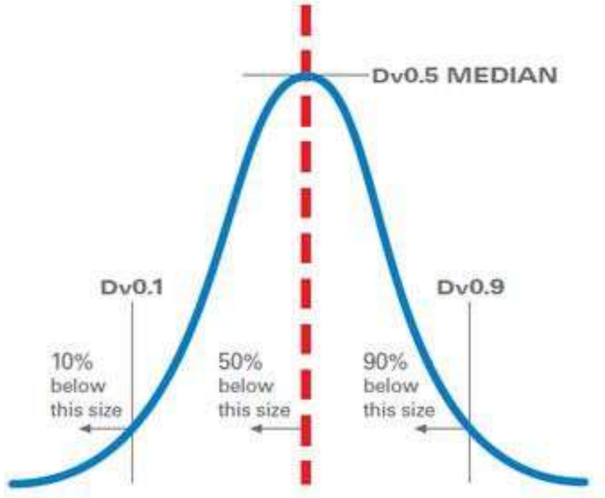


Fig 2.1. Particle size distribution | Normalized curve

Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The angular scattering intensity data is then analysed to calculate the size of the particles responsible for creating the scattering pattern, using the Mie theory of light scattering. The particle size is reported as a volume equivalent sphere diameter. Particle size distribution can't be expressed by a single value as Average particle size since it is a range of values thus it is denoted by d10, d50 and d90 [16].

$$\text{Span} = d_{90} – d_{10} / d_{50}$$

The average grain size measurement could be done using a instrument of FSSS which is a acronym of Fisher Sub Sieve Sizer, the average particle size instrument works on the principle of air permeability between the particles, so based on the difference between the inlet and the outlet air passed along with the calculation of the time, the average particle size is determined. The air permeability method of particle size measurement has the advantage of being fast and easy to perform, taking just a few minutes without a great deal of sample preparation. In this method, a quantity of powder equal to 1 cm3 of actual solid material (sample mass numerically equal to the density of the material) is packed to a specified force in a tube of known inside diameter. The porosity of the powder bed is then measured by means of the height of the powder column, thereby measuring the total (apparent) volume of the powder bed and comparing that to the 1 cm3 of material in the tube. Air is then passed through the powder bed at a specified pressure, and the transmitted pressure is measured. The specific surface area of the powder is then determined using the Kozeny-Carman equation, which relates the surface area to the porosity and the pressure drop through the compacted powder.

In FSSS or SAS (Sub sieve Auto sizer), we can only determine the average particle size which is of single value, where the value is a kind of approximation. To overcome this method of particle size distribution techniques has been emerged to study the entire range of particle size in a taken sample which gives the idea of different grain size of the particle present in the sample. The regular production batches of W are taken for study, small amount of homogenized sample collected for analysis of PSD. In parallel FSSS data collected from production for comparison. The below are the average of 20 lower grain size grade W powder homogenized results.

	d10	**d50**	**d90**	**Span**	**FSSS**
Average	0.76575	2.0346	5.0926	2.124	1.267

Table 2.2.Avg. current level performance of PSD & FSSS

After every trial pass through furnace, approx. 3mm of W samples are collected in top and bottom layers for comparison to study the difference. Also, the same is collected in three different locations such as left, middle and right to study the lengthwise effect in reduction boat. From the previous study as well as initial trials it is observed that there is a grain size difference between the top and the bottom layers, the top layers have smaller grains whereas bottom layers have larger grains. This majorly led to the wide spread of the particle size distribution.

	D10	**D50**	**D90**	**Span**
Top	**0.624**	**1.27**	**2.417**	1.412
Bottom	**1.39**	**3.335**	**8.207**	2.044

Table 2.3. Comparison of Top and Bottom Layers

The most influential parameters which lead to wide PSD include thermal conductivity, powder bed thickness and raw material particle size distribution, that can be done trials and experimental studies without affecting the whole production lot, instead with individual units.

3.1 Control Of Thermal Conductivity

Proposal 1: Removal of already reduced Tungsten layers attached to the boat

Over a period after continuous cycles of operation, It is observed that already reduced tungsten gets attached to the surface of the boat and formed as flakes with thickness of around ~ 1.5mm, further WO_3 powder is filled once again above the flakes of layers. It is known that metallic Tungsten has high thermal conductivity compared to the cast steel (Boat material), thus there is huge chances of bottom layer having more growth and getting coarser as a effect of high amount and rate of heat transfer.

Thermal Conductivity	
SS309 (Cast SS boat)	15.6 W/mK
Tungsten	112 W/mK

Table 2.4. Thermal Conductivity of investigated materials

Proposal 2: Adding a steel plate in between the boat with air gap below.

The possibilities are explored to still reduce the thermal conductivity of the reduction boat. Thus it is suggested to place a sheet metal of same dimensions of the boat at a certain height with a air gap in between to reduce the thermal effect in the bottom layers.

Thermal Conductivity	
SS309 (Cast SS boat)	15.6 W/mK
SS304 (Middle Plate)	16.2 W/mK
Air	0.024 W/mK
Hydrogen	0.172 W/mK

Table 2.5. Thermal Conductivity of SS309, SS304,Air&H2

It is proposed such that the heat transfer quotient will be reduced in this condition such that the heat will flow through boat then through air and then SS304 plate added, then to the bottom layer so that there will be reduction in the direct conduction mode of heat transfer.

3.2 Control Of Powder Bed Thickness

Proposal 1: Even spread of the tungsten oxide powder layer.

In the actual production process the tungsten oxide is filled to the reduction boat by a automated process with the help of hopper which is PLC programmed. While filling the powder takes the form of a hump in the reduction boat which has high bed thickness in the middle and less in the sideways, this has the high impact on reducing the uniformity of the reduced W grain size.

Proposal 2: To increase the width of the boat to have lower bed thickness

By increasing the width of the boat, it is possible to have lower bed thickness so that we can obtain narrow particle size distribution. This has less implementation feasibility since lowering the bed thickness changes the average particle size (FSSS) so that other parameters to be optimized to obtain the desired FSSS. Also, in real condition there is a undulations in the furnace tube because of which the boat may get struck inside and jammed if designed like below with tight tolerance. The possibilities of implementation to be further explored with extensive study.

3.3 Control of original particle size distribution

Proposal 1: Ball milling of raw material tungsten oxide powder

The imported tungsten oxide YTO/BTO used has PSD of the range of 3 to 50 microns which is a huge difference compared to the output of the metallic Tungsten PSD which has the range of 0.6 to 6 microns for lower grade and 0.9 to 10 microns for higher grade. So as a part of experimentation it is proposed that by reducing the variation in the raw material PSD, it is possible to have the effect of narrow PSD in the output. So it is decided to ball mill the raw material of Blue tungsten oxide for 5 hours to reduce the grain size as well as distribution span and check the difference in output metallic tungsten W. The experimentation is under progress and to be intensively carried later.

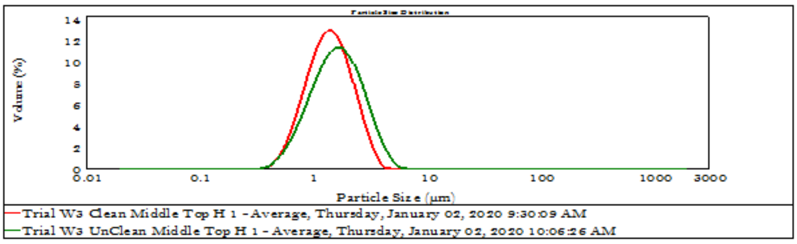
4. RESULTS & DISCUSSIONS

The proposals discussed are conducted experimentally by controlling the reduction conditions such as cleaning of the reduced flakes, boat design, raw material distribution in the boat is explored and followed by results are interpreted.

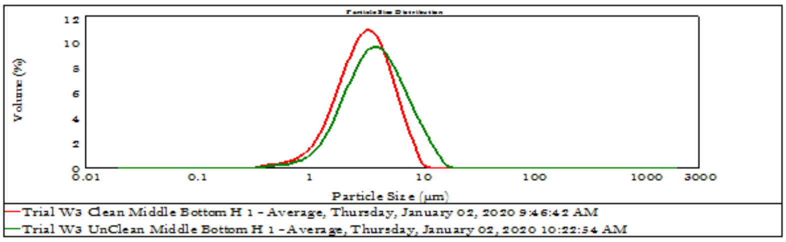
(i) Removal of reduced tungsten layers attached to the boat

After reduction the samples are collected in top and bottom layers and taken for PSD analysis.

Clean and Unclean Boat | Middle Portion | Top & Bottom

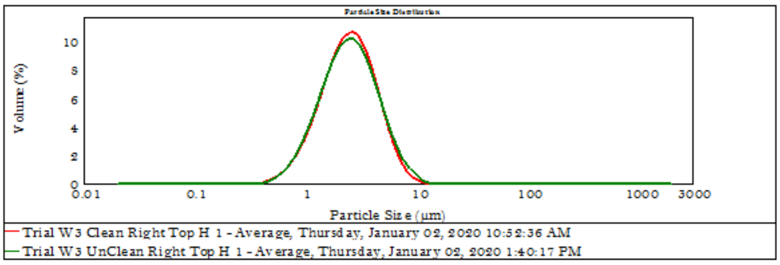


		D10	D 50	D90	Span
Top	Clean	0.767	1.393	2.454	1.211
	Unclean	0.816	1.631	3.094	1.397

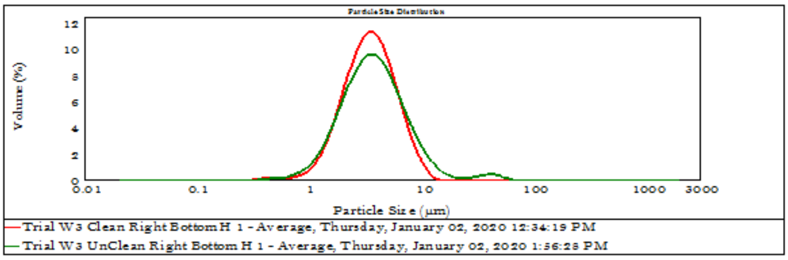


		D10	D 50	D90	Span
Bottom	Clean	1.493	3.21	6.178	1.459
	Unclean	1.748	3.946	8.721	1.767

Clean and Unclean Boat | Right Portion | Top & Bottom

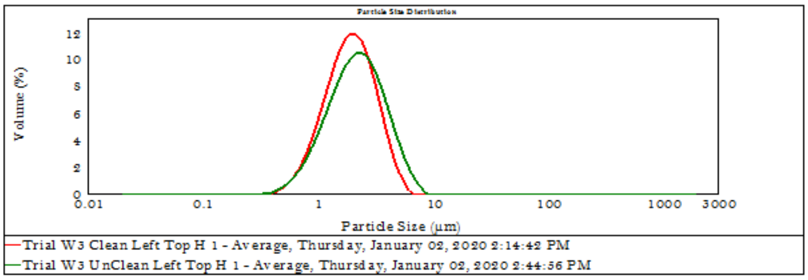


		D10	D50	D90	Span
Top	Clean	1.129	2.438	4.899	1.546
	Unclean	1.118	2.441	5.158	1.655

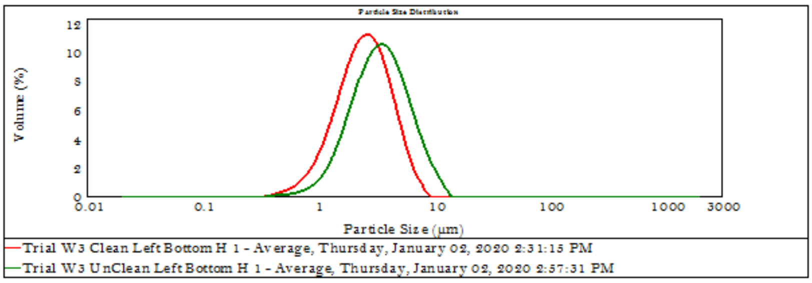


		D10	D50	D90	Span
Bottom	Clean	1.714	3.455	6.696	1.442
	Unclean	1.642	3.666	8.614	1.902

Clean and Unclean Boat | Left Portion | Top & Bottom



		D10	D50	D90	Span
Top	Clean	0.983	1.946	3.575	1.332
	Unclean	1.015	2.207	4.434	1.549



		D10	D 50	D90	Span
Bottom	Clean	1.179	2.475	4.717	1.429
	Unclean	1.609	3.404	6.958	1.572

Figure 3.1: PSD of the homogenized powders Batch 2918

Based on comparative study, it is observed that the d50 of all unclean boats are greater than cleaned boats, which clarifies due to the presence of the tungsten layer of flakes which has higher thermal conductivity than cast steel, there is a growth in the overall particle grain size. Also, there is a average reduction in span between the uncleaned and cleaned boat by 14%. The above are the comparison study done by top and bottom layers. In addition, the entire boat samples has to be collected and homogenized and checked for cleaned and uncleaned boat which is to be done in future work.

(ii) Adding steel plate in between the boat with air gap below

Initially the trials are taken by placing thin sheet of SS304 which is of 0.8mm, thickness on the supporting legs in both corners of the boat and taken trial, but there seems to be gaps available in the sides of the plates which leads to some quantity of powder fell below the plates, that may not provide precise results. As a corrective measure the side gaps are closed with the cladding cloth of tungsten carbide, but during reduction at high temperature the cladding cloth gets turned into powder form and again some quantity of powders felt below the plate. In addition, because of the thin sheet metal plate exposed to higher temperature of 900ºC, the plate gets sagged. Finally, the thick plate of 4mm SS310 plate fabricated to exact boat dimensions and completely welded throughout the side gaps. In addition to avoid sagging thick alumina bricks (low thermal conductivity) of 20mm is placed below the plate and exactly the plate is placed touching above alumina. In these experiments the comparison is done with Regular boat (with hump like WO3 powder profile while loading through hopper), Evenly distributed boat by shaking or vibration and the plate added boat.

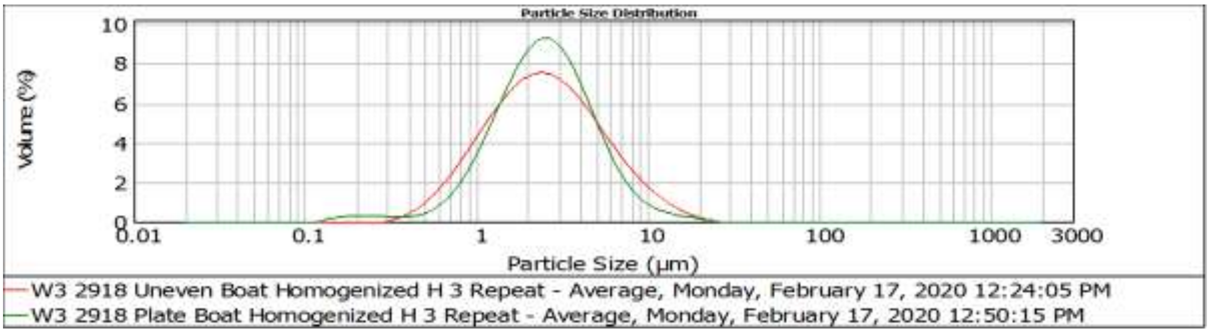
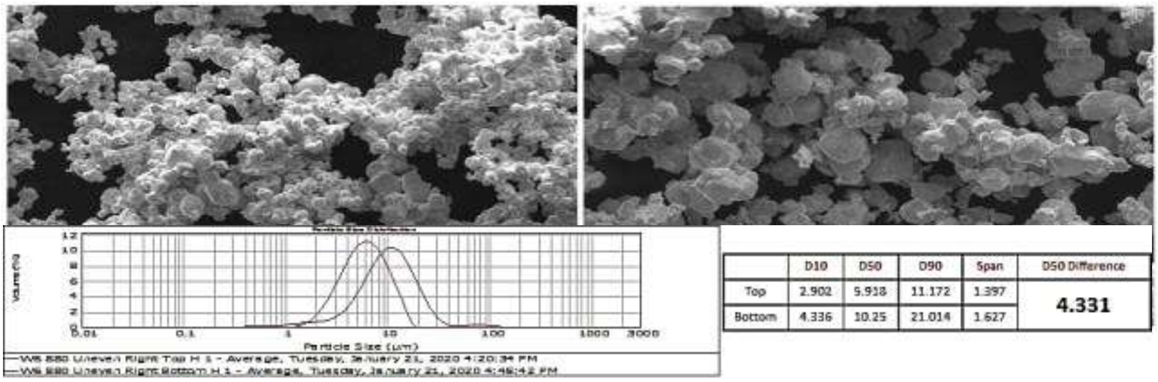


Fig: 3.2. Homogenized PSD results comparison 2918

	d (0.1)	d (0.5)	d (0.9)	Span	D43	D32
W3 2918 Uneven Boat Homogenized	0.903	2.446	6.955	2.474	3.364	1.855
W3 2918 Even Boat Homogenized	0.939	2.544	7.084	2.416	3.553	1.852
W3 2918 Plate Boat Homogenized	1.012	2.45	5.657	1.897	3.064	1.737
W3 2918 Overall Batch Homogenized	**0.797**	**2.203**	**5.959**	**2.343**	**2.948**	**1.534**

Table 3.1. d10,d50 and d90 values of the homogenized powders Batch 2918

Plate added Boat:



	D10	D50	D90	Span	D50 Difference
Top	2.902	5.918	11.172	1.397	4.331
Bottom	4.336	10.25	21.014	1.627	

Fig 3.4. SEM image & PSD of Top and Bottom layer Comparison | Regular Boat From the above results, it is clearly seen that there is a reduction in the distribution span by 23%, on adding the plate in between the boat to reduce the thermal effect, without much variation in the d50. Thus it shows that thermal conductivity has a impact on the PSD and it could be controlled by exploring materials / geometry that tends to exhibit low thermal conductivity.

Trial 2: Batch 2921

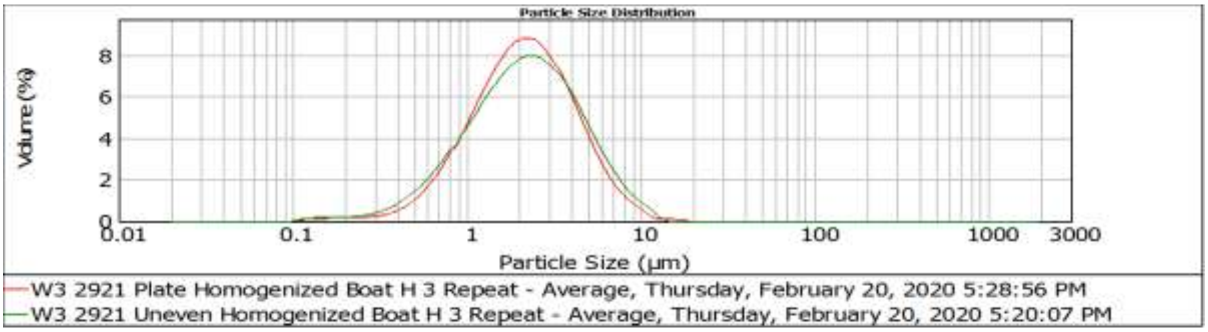


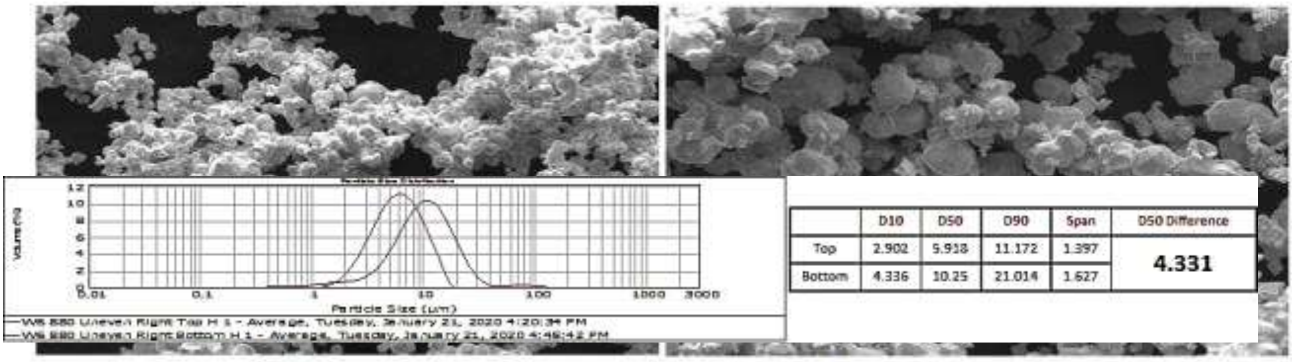
Fig: 3.3. Homogenized PSD results comparison 2921

Sample Name	d (0.1)	d (0.5)	d (0.9)	Span	D43	D32
W3 2921 Uneven Homogenized Boat	0.77	2.193	5.491	2.153	2.755	1.517
W3 2921 Plate Homogenized Boat	0.848	2.138	4.984	1.934	2.621	1.554

Table 3.2. d10, d50 and d90 values of the homogenized powders Batch 2921

From the above results of PSD, it is clear that there is a reduction in distribution span by 10% for plate added boat, which in turn confirms the influence of thermal effect on bottom layers. In parallel the cross check has been done with the SEM Images of the Top and bottom layers of Regular boat and plate added boat.

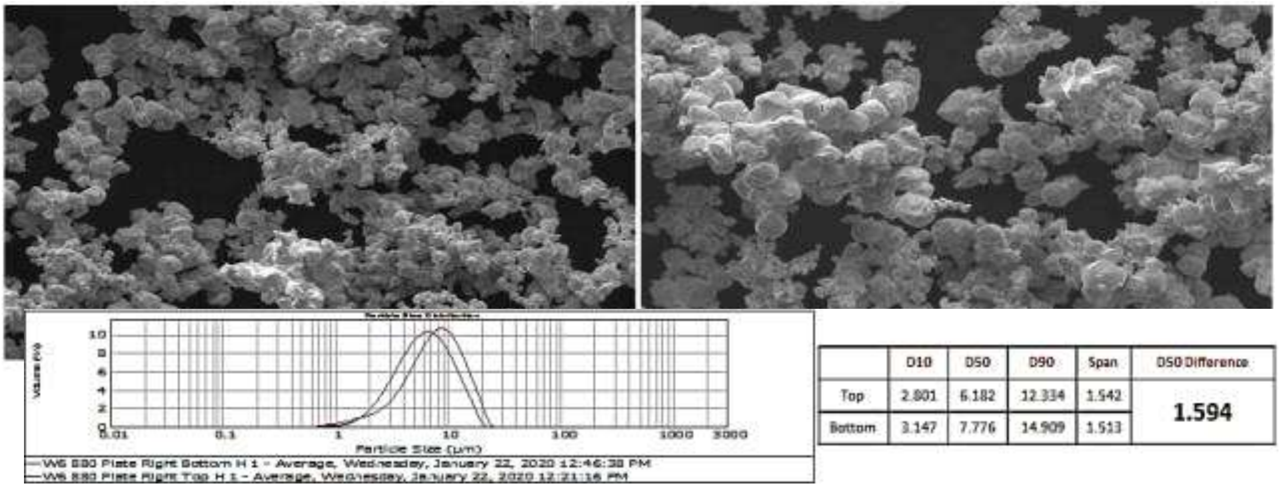
Regular Boat | Uneven Boat:



Top Layer W Powder

Bottom Layer W Powder

Fig 3.4. SEM image & PSD of Top and Bottom layer Comparison | Regular Boat



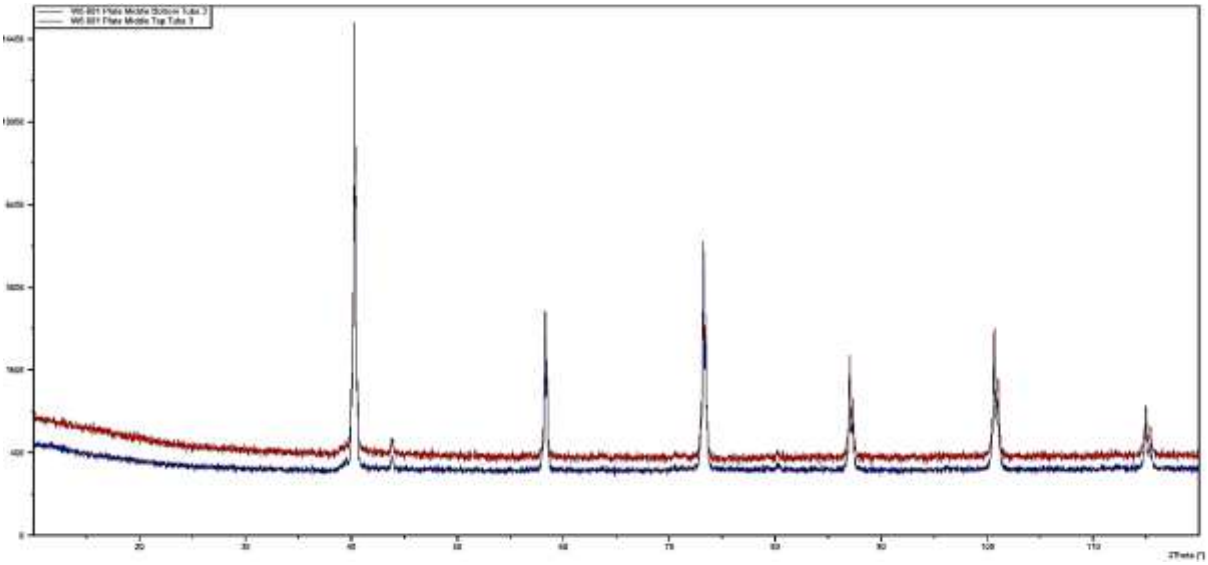


Fig 3.6. XRD results of Top and Bottom layers for the boat with plate added

XRD results confirm the complete reduction occurred in both top and bottom, and there is no presence of any other phases or other compounds. Similarly, Oxygen and Nitrogen analysis done to cross check for the presence of unreduced oxide phases, which confirms the oxygen limit is under specification limit of negligible value.

Layer	Weight(g)	%Oxygen	%Nitrogen
Top	0.0684	0.0519	-0.00054
Bottom	0.091	0.0198	0.0096

Table 3.3. Oxygen and Nitrogen analysis results for Top and Bottom layers for plate added boat

4. CONCLUSION

1. The study of reduction mechanism (Chemical vapour transport) of tungsten oxide to metallic tungsten provides insight on the influencing parameters that leads to uneven grain growth and wide distribution span, due to difference in grain size between top and bottom layers. It is come to know that powder bed thickness and thermal conductivity effect in the bottom layers has crucial importance in controlling the particle size distribution. Thus, solutions have been explored to have uniform bed thickness as well as optimum thermal effect in the bottom layers.
2. The modification trial suggestion of plate addition in between the boat with air gap/alumina bricks has shown significant results in reducing the distribution span from the current level of performance. Also, by cleaning / scrapping the flaky layers of the tungsten attached to the surface of the boat it is highly feasible to reduce the thermal effect on the bottom layers.
3. In addition, by shaking or vibrating the boat after powder feed from hopper makes the uniform distribution of powder layers in the boat, without a hump like profile of

powder distribution, so that after reduction it is feasible to obtain narrow distribution of particle size compared to as it is condition. In addition, the repeatability and reproducibility of the above experimental results to be established further by performing multiple repetition of trials. There are other number of possible solutions to control the distribution span which is explored in the future work.

Acknowledgment
The entire project work has been carried out in Kennametal India Private Limited, Bangalore. Kennametal is an American supplier of tooling and industrial materials founded in 1938 by Philip M. McKenna in Latrobe, Pennsylvania area. Kennametal India Private Limited is a key manufacturer of cemented carbide and other machine tools components which are being supplied to various sectors of engineering practice such as Aerospace, Defence, Automotive and in major heavy industries.

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