10
-25-75

OL-1399

UCRL-51812

CHARACTERIZATION OF ASTM ROUND-ROBIN TUNGSTEN-POWDER SAMPLES

Charles A. Slettevold

Arthur H. Biermann

May 15, 1975

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

MASTER

REPRODUCTION OF THIS DOCUMENT UNLIMITED

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$ *; Microfiche \$2.25

<u>*Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60

LAWRENCE LIVERMORE LABORATORY
University of California, Livermore, California, 94550

UCRL-51812

**CHARACTERIZATION OF ASTM ROUND-ROBIN
TUNGSTEN-POWDER SAMPLES**

Charles A. Slettevold
Arthur H. Biermann

MS. date: May 5, 1975

—NOTICE—

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

49

Contents

Abstract	1
Introduction	1
Types of Analysis and Equipment	1
Initial Sample Handling	1
Methods and Results	2
Micrographs	2
Apparent-, Tap-, and True-Density Determinations	2
Apparent Density	2
Tap Density	3
True Density	3
Surface-Area Analysis	4
Average Size by the Fisher Sub-Sieve Method	4
Weight Distribution by Centrifugation	4
Weight Distribution by the Coulter Counter	6
Number Distribution by Light Microscopy and Image Analysis	6
Summary of Results	7
Acknowledgments	8
Appendix A. Lazy-Susan Sample Splitter	9
Appendix B. Micrographs	11
Appendix C. Particle-Size Distributions and Surface-Area Measurements	13

CHARACTERIZATION OF ASTM ROUND-ROBIN TUNGSTEN-POWDER SAMPLES

Abstract

The Lawrence Livermore Laboratory (LLL) Particle Characterization Laboratory Group has participated in an industry-wide round-robin investigation aimed at the characterization of tungsten powder. The round-robin series is sponsored by the ASTM Subcommittee on Refractory-Metal Powders (B-09.3). The analyses performed at the suggestion of the ASTM

subcommittee included measurements of tap density, apparent density, true density, average particle size, and surface area. We also performed determinations of particle-weight and size distributions, and conducted particle inspection by microscopy. This report describes the equipment and procedures used and summarizes the results of these analyses.

Introduction

This report presents the results of tests performed by the Lawrence Livermore Laboratory (LLL) Particle Characterization Laboratory Group of the Chemistry and Materials Science Department on five samples of tungsten powder. These samples were supplied to LLL as part of the Laboratory's participation in an

industry-wide round-robin effort aimed at the characterization of tungsten-metal powder. This effort is sponsored by the ASTM Subcommittee on Refractory-Metal Powders (B-09.3) as part of its effort to develop a standard reference powder and to compare currently unstandardized techniques.

Types of Analysis and Equipment

The equipment used and types of analyses performed as part of our participation in this characterization study are listed

in Table 1. Any variances from standard ASTM procedures are indicated in the discussions of methods and results.

Initial Sample Handling

The ASTM subcommittee sent LLL five tungsten-metal-powder samples which

were numbered 196 through 200. These were the LLL portion of the samples sent

Table 1. Equipment used for characterization.

Type of analysis	Equipment
Tap density	Tap-Pak Volumeter J. Engelmann A.G. Model JEL 572
Apparent density	Carney funnel
True density	Huckman Air-Comparison Pycnometer (helium-air) Huckman Instrument Corp. Model 930
Surface area	Orr Surface-Area Analyzer (Nitrogen adsorption) Micromeritics Instrument Corp. Model 2100A
Average size	Fisher Sub-Sieve Sizer Fisher Scientific Co. Model 14312
Particle-weight distribution	Centrifuge and Viewer Mine Safety Appliance Co. Centrifuge: Model HC 78640. Viewer: Model 79210
Particle-number distribution	Counter Counter Coulter Electronics Co. Model II Light microscope interfaced to image analyzer Quantimet Image Analyzer Imasco Corp., a Division of Metals Research Industries (U.S.)
Micrograph analysis	Light microscope Scanning electron-microscope Transmission electron-microscope (Other equipment: Ultrasonic probe for mixing: Biosonik Probe Biosonik Scientific Co. Model BHO-II)

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Energy Research and Development Administration to the exclusion of others that may be suitable.

Methods and Results

MICROGRAPHS

Micrographs of sample No. 196 were taken using a light microscope, a transmission electron-microscope, and a scanning electron-microscope. These are shown in Appendix B (Figs. B-1 through B-5). The presence of agglomerates in the sample is apparent in these photographs. Cubical and other polygonal shapes of tungsten particles were encountered.

APPARENT-, TAP-, AND TRUE-DENSITY DETERMINATIONS

Apparent Density

Apparent density was measured by the Carney method in accordance with ASTM

to all the participants in the round-robin characterization effort. After receipt, the five samples were opened and quickly transferred into the entry port of a high-purity-argon glove-box line. The port was evacuated to less than 2.66 Pa pressure and back-filled with an argon atmosphere containing less than one ppm of either oxygen or water vapor. This was done three times. All sampling and some of the analyses were performed in an argon-filled glove box. A "lazy-susan" sample splitter (described in Appendix A), was used to separate samples for the various tests into the approximate sizes needed. Before any tests were made in which moisture would be a factor, all samples were baked at 100°C in a vacuum oven for about 16 hours.

specification B-417-64. However, in a previous modification, our cup had one inch removed from its height, thereby reducing its volume to less than half of the original.

Dried tungsten powder was placed in the Carney funnel. A cup of known weight and volume was placed into a keyed position under the funnel and the ball swung away from the stem. The powder flowed or was aided in flowing until overflow. The top of the cup was then scraped with a straightedge to remove excess material. The cup was tapped lightly to prevent loss of material in further handling, and its weight was determined. This procedure was repeated three times and an average

weight established from which the average apparent density was calculated. The results of the five samples are presented in Table 2.

tapped 3000 times. The volume was read and the weight of tungsten determined. Results of three tests made on each of the five samples are given in Table 3.

Tap Density

In accordance with ASTM specification B-527-70, 50 grams of tungsten powder were added to a 25 ml graduated cylinder, placed on a Tap-pak volumeter, and

True Density

An air-comparison pycnometer was used to determine the true density of the powder samples. A 60- to 70-gram sample of dried tungsten powder was

Table 2. Apparent densities.

Sample	Weight No. 1 (g)	Weight No. 2 (g)	Weight No. 3 (g)	Average (g)	Apparent density (Mg/m ³)
196	25.387	25.502	25.263	25.384	2.432
197	25.138	25.066	24.978	25.061	2.401
198	24.602	25.243	24.528	24.791	2.375
199	25.581	25.818	25.520	25.640	2.456
200	25.597	25.327	25.640	25.521	2.445
Average Apparent Density					2.422

Table 3. Tap densities.

Sample No.	Trial No.	Weight (g)	Volume (ml)	Density (Mg/m ³)	Average density for each sample (Mg/m ³)
196	1	50.0670	11.7	4.2792	4.25
196	2	49.8160	11.75	4.2396	
196	3	50.0100	11.85	4.2202	
197	1	50.2074	11.8	4.2548	4.26
197	2	50.0352	11.75	4.2584	
197	3	50.2362	11.8	4.2573	
198	1	49.110	11.65	4.2842	4.29
198	2	50.2775	11.7	4.2972	
198	3	50.0501	11.65	4.2961	
199	1	50.1522	11.5	4.3610	4.35
199	2	50.0402	11.5	4.3513	
199	3	49.6928	11.45	4.3399	
200	1	49.8490	11.65	4.2788	4.28
200	2	50.1765	11.75	4.2703	
200	3	50.1145	11.7	4.2832	
Overall average density for the five samples					4.2847

placed in the pycnometer cup and the volume measured three to four times. The sample was then weighed and a dense stainless steel ball of approximately the same volume as the sample was placed in the cup and measured. An appropriate correction factor was determined using the known volume of the ball. All five samples were tested. Results are tabulated in Table 4.

Table 4. True densities.

Sample No.	Measured volume (ml)	Weight (g)	Density (Mg/m ³)
196	3.44	66.2827	19.27
197	3.39	64.8605	19.13
198	3.42	65.0680	19.32
199	3.37	64.4785	19.13
200	3.37	64.5120	19.14
Average density of all five lots			19.20

SURFACE-AREA ANALYSIS

Twenty- to thirty-gram samples were used for the static (non-flowing) nitrogen-adsorption surface-area determination. The samples were baked under vacuum for four hours at about 220°C prior to making the determinations.

Brunauer-Emmett-Teller (BET) adsorption isotherms were generated using from 7 to 12 points of partial pressure. From the resulting slope and intercept, the surface area was calculated and the particle size of an average equivalent sphere was determined.

In Table 5, these values are shown for the five samples. A typical BET adsorption curve is given in Appendix C (Fig. C-1).

AVERAGE SIZE BY THE FISHER SUB-SIEVE METHOD

Results of Fisher Sub-Sieve analysis for samples No. 197 and No. 200 are presented in Table 6. The equipment was calibrated with a sub-sieve calibrator (serial number 1160) with the porosity set at 0.75. The high reading of 5.15 and low reading of 2.01 were accurate within the reading ability of the sizer.

WEIGHT DISTRIBUTION BY CENTRIFUGATION

The Whitby sedimentation method, which was used for these determinations, requires four centrifuges and a viewer.

Table 5. Results of surface-area analysis.

Sample No.	Intercept	Slope	Surface area (m ² /g)	Standard deviation	Calculated diameter (μm)
196	0.09157	7.0203	0.612	0.00175	0.51
197	0.087642	6.9913	0.615	0.00155	0.51
198	0.090111	7.0438	0.610	0.00122	0.51
199	0.10171	6.7347	0.637	0.00280	0.49
200	0.10344	6.8121	0.629	0.00451	0.50
Average surface area			0.621		

Table 6. Fisher sub-sieve average particle size.

Sample	Porosity	Average diameter (μm)
197	0.80	1.43
200	0.80	1.43

See Fig. 1. The centrifuge tubes, which are of a special design, have a 0.7 mm capillary at the bottom of each.

The samples were first split to near the needed size for the analysis using the LLL lazy-susan sample splitter (see Fig. A-1). In this analysis we used the Mine Safety Appliance (MSA) sample scoop, which is designed to give a proper-sized sample. The narrow size distribution of the samples made it necessary to use a lower

concentration of powder than would have been necessary for more heterogeneous samples. This is due to the narrow time range within which a majority of the particles fall, thereby causing a high-concentration zone in the sedimentation liquid. This tended to lead to reagglomeration and a biasing of data to the upper sizes.

The sedimentation fluid used in this analysis consisted of water containing 0.1% Daxad No. 23 as a dispersant. The samples were prepared by dispersing the powder in 1 ml of a feeder liquid consisting of 70% sedimentation fluid and 30% acetone. The suspension was first ultrasonically mixed using a small tip on a Biosonic probe and then stirred on a vortex mixer until ready for use. The

Fig. 1. Centrifugal sedimentation equipment for determination of particle-weight distribution.

sample was placed in the feeder chamber and hand mixed until it was layered out on the surface of 10 ml of sedimentation fluid contained in the centrifuge tube.

According to a predetermined schedule of times and centrifuge speeds, the height of the powder sediment in the capillary of the centrifuge tube was measured on the viewer. Each sedimentation time corresponded to a certain Stoke's diameter based on an assumed spherical particle. A minimum of two trials per sample were made. Further samples were run until agreement of results was reached. A computer plot of the cumulative weight distribution and a weight-distribution histogram are shown in Appendix C for sample No. 196. A summary of the distributions for samples 196 to 200 is given in Table 7.

WEIGHT DISTRIBUTION BY THE COULTER COUNTER

A Coulter Counter with a 50 μ m aperture was used for determination of particle-weight distribution. In preparation for analysis, the samples were rubbed in electrolyte (1% isoton) on a small watch glass. The dispersed powder was then added to a beaker containing more electrolyte and ultrasonically mixed using a sonic probe. To keep the larger particles and aggregates suspended, stirring was maintained throughout the counting period. Total counts for the various samples ranged between 2,000 and 14,000 particles. The 20th, 50th, and 80th percentiles of the cumulative-weight percentage below stated size are listed in Table 8. Appendix C (Figs C-2 through C-9) gives examples of computer-generated output showing cumulative percent by weight

Table 7. Particle diameters corresponding to the 20th, 50th, and 80th percentiles of the weight distribution as determined by centrifugal sedimentation.

Sample No.	Maximum particle diameter (μ m) for indicated percentile		
	Lower 20% by weight	Lower 50% by weight	Lower 80% by weight
196	3.3	5.7	8.5
197	3.3	5.2	9.0
198	2.1	3.4	4.7
199	2.3	3.5	5.0
200	4.8	6.1	10.8

Table 8. Particle diameters corresponding to the 20th, 50th, and 80th percentiles of the weight distribution as determined by Coulter-Counter analysis.

Sample No.	Maximum particle diameter (μ m) for indicated percentile		
	Lower 20% by weight	Lower 50% by weight	Lower 80% by weight
196	2.5	3.8	5.8
197	2.3	4.0	6.0
198	2.8	4.2	8.5
199	2.8	3.7	10.0
200	3.6	4.5	5.9

below stated size and weight-distribution histograms for samples 196 and 199.

NUMBER DISTRIBUTION BY LIGHT MICROSCOPY AND IMAGE ANALYSIS

The LLL particle-characterization facility employs an image-analysis system (Fig. 2) for determination of particle-size distributions. This system

Fig. 2. Image analysis facility.

can be interfaced to a light microscope with an automatic stage-advance, a scanning electron-microscope, or an epidiastcope for evaluation of pictures or negatives.

For size determination of the five LLL round-robin tungsten samples the light microscope system was used with size classification depending on the projected area of the tungsten particles. First, tungsten samples were dispersed in immersion oil on slides by means of a 2-mm diam wooden dowel. Each slide was then placed on the microscope stage and a magnification was chosen. Between 1400 and 3000 particles were counted and sized for each sample. The counting of

many agglomerates was eliminated by using the pattern-recognition feature of the image analyzer. Computer results of the image analysis include plots of percent number versus equivalent spherical diameter, and a calculated weight versus equivalent spherical diameter. A cubical shape-factor was used in the calculations. Plots include both cumulative percent below stated size and histogram distributions. Table 9 lists summary cumulative percent data for the five samples. Typical computer output is included in Appendix C. In Table 9, note that because of variation between samples some analyses were repeated.

Summary of Results

• The average apparent, tap, and true densities of the five round-robin tungsten

samples Nos. 196 to 200, were 2.423, 4.285, and 19.2 Mg/m³, respectively. The

Table 9. Particle diameters corresponding to 20th, 50th, and 80th percentiles for the cumulative number and weight distribution as determined by image analysis.

Sample No.	Maximum particle diameter (μm) for indicated percentile						Magnification (X)
	Lower 20% by number (frequency)	Lower 50% by number (frequency)	Lower 80% by number (frequency)	Lower 20% by weight (calculated)	Lower 50% by weight (calculated)	Lower 80% by weight (calculated)	
196	1.3	2.3	3.8	4.0	7.0	9.5	500
196	1.4	2.3	3.9	3.4	5.0	6.5	312.5
196	0.9	1.6	2.6	2.5	3.6	8.0	500
197	1.0	1.7	2.5	2.5	3.5	4.7	500
197	1.0	1.6	2.6	2.3	3.2	4.4	500
198	1.2	2.3	3.8	3.6	6.0	15.0	500
199	1.7	2.7	4.7	3.8	5.8	8.5	312.5
200	1.3	2.1	3.9	3.3	4.5	5.8	312.5

average surface area determined by nitrogen adsorption was $0.621 \text{ m}^2/\text{g}$. These particle-characterization measurements varied little in the five samples tested.

• Larger variations were encountered in measuring the particle size distributions using the centrifugal-sedimentation, Coulter-Counter, and microscope-image analysis. The variations in size distributions may be caused by nonrepresentative sampling since very small sample amounts are required for these analyses. Size variations can also be attributed to the large number of aggregates present, as shown by the micrographs.

• The particle diameters by microscope-image analysis corresponding to the 50th percentile by number ranged from 1.6 to $2.7 \mu\text{m}$. Weight distributions from microscope-image analysis, as calculated from number distributions, were in the range of sizes determined from direct weight-distribution measurements.

• The spread of particle diameters corresponding to the 50th percentile by weight, were 3.2 to $5.0 \mu\text{m}$ by microscope-image analysis; 3.7 to $7.2 \mu\text{m}$ by centrifugal sedimentation; and 3.7 to $4.5 \mu\text{m}$ by use of the Coulter Counter.

Acknowledgments

The authors' gratitude is extended to Roy O. Lindahl and Carol M. Weaver for their work in the particle characterization of these samples.

Appendix A

Lazy-Susan Sample Splitter

The LLL lazy-susan sample splitter (Fig. A-1) has been developed to divide a powder sample into small but representative fractions of the original. The device, consisting of an eight-inch pan housing eight pie-shaped pans, is mounted on a variable speed rotating table. Extending upward through the eight-inch pan is a rod which provides stationary support

for a lucite cover, a vibrator, a feeder trough, and a funnel.

The rate of flow of the powder, which is related to such factors as shape, particle size, static charge, and moisture, can be regulated by the vibration and clearance between the funnel tip and the feed trough. The rotation rate determines the quality of the separation.

Fig. A-1. LLL Lazy-susan sample splitter.

Appendix B

Micrographs

Figures B-1 through B-5 are photographs of sample No. 196 as viewed by (a) light microscopy, (b) transmission electron microscopy, and (c) scanning electron microscopy.

Fig. B-1. Sample 196 viewed by light microscopy (820X).

Fig. B-2. Sample 196 viewed by transmission electron microscope (1250X).

Fig. B-3. Sample 196 viewed by transmission electron microscope (12,500X).

Fig. B-4. Sample 196 viewed by scanning electron microscope (2000 X).

Fig. B-5. Sample 196 viewed by scanning electron microscope (2000X).

Appendix C

Particle-Size Distributions and Surface-Area Measurements

Figures C-1 through C-9 are computer-generated diagrams showing selected particle-size distributions resulting from surface-area analysis, centrifugal-sedimentation analysis, Coulter-Counter measurements, and microscopy-image analysis.

Fig. C-1. Sample 196. BET isotherm from surface-area analysis, where p = partial pressure of gas; p_s = saturation pressure of gas; and V_a = volume of adsorbed gas.

Fig. C-2. Sample 196. Cumulative weight distribution by Coulter-Counter analysis.

Fig. C-3. Sample 196. Weight distribution by Coulter-Counter analysis.

Fig. C-4. Sample 196. Cumulative weight distribution by centrifugal sedimentation.

Fig. C-5. Sample 196. Weight distribution by centrifugal sedimentation.

Fig. C-6. Sample 199. Cumulative size distribution by number, from image analysis using light microscopy.

Fig. C-7. Sample 199. Number distribution by image analysis using light microscopy.

Fig. C-8. Sample 199. Cumulative weight distribution as calculated from the number distribution (from image analysis using light microscopy).

Fig. C-9. Sample 199. Weight distribution as calculated from the number distribution (from image analysis using light microscopy).