Evaluation of a New Source for Powdered and Granular Zirconium

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Outline

- Background
- Analytical and Testing Methods
- Analyses, Comparisons with MIL-Z-399D (Section 3) , CoAs, and Results and Ignition Gain
- Conclusions and Recommendations

Background

- In recent years, the Zirconium (Zr) supply industry has shrunk and presently there is only one manufacturer of this elemental powder meeting Military Specification Zirconium (granular and powdered) MIL-Z-399D.

- Albemarle (formerly Chemetall and Rockwood Lithium) in Germany is the only qualified supplier of MIL-Z-399D Type II Class 1 Zr and Type II Class 2 Zr. Unfortunately, Albemarle no longer provides Zr granular Type I Class 2, therefore those applications that require this type of Zr are directly affected.

- Chemadyne LLC, is a distributor of different types of Zr powders manufactured by Shree Babaji Chemicals Pvt. Ltd located in India. This Zr source offers all types and classes of MIL Z 399D granular and powdered material, including Type I Class 2.

- Some of analytical methodologies listed as quality assurance provisions in MIL-Z-399D - Section 4 are outdated and should be replaced with more modern analytical techniques that have become a part of the Zr manufacturing industry standard and are utilized to provide the results listed in the certificates of analyses. However, Section 4 of the MIL-Z-399D has not been updated to include them.

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Background (Con't)

Objective

This presentation will focus on full characterization of granular and powdered Zr samples using: IPC, TGA/DSC, BET, SEM/EDS, and burn rate testing then comparison of the results with the MIL-Z-399D (Section 3) requirements.

Analytical and Testing Methods

Zirconium Characterization

For the full characterization of sampled Zr powders the following methods were used:

1. **Microstructure** – Scanning Electron Microscopy (SEM) Zeiss Supra 40 (see Appendix A). This procedure is not required by MIL-Z-399D and Albemarle, however, it provides important information on morphology of Zr powders.

2. **Particle Size Distribution** – MicroTrac 3000. Laser diffraction technique is commonly used for more than 30 years to determine particle size distribution of metallic and ceramic powders in the range from submicron to hundreds of microns. The laser diffraction technique provides accurate average particle size of powders. Therefore, the Blaine test is not commonly used anymore for determination of average particle size. At this point, only the cement industry is using this technique.

Analytical and Testing Methods

Zirconium Characterization(con't)

3. **Specific Surface Area** – BET Method – Gemini 2360 from Micromeritics Co.

4. **Elemental Analysis** of Constituents, like Ca, Fe, Al, Cl, Si, and Sn - Inductively Coupled Plasma (ICP) and Atomic
   Emission Spectroscopy – conducted by Galbraith Laboratories

5. **Hydrogen Content** – Hot Vacuum Extraction conducted by the Luvak Laboratories

6. **Sieve Analysis for Type I Class 2 Zr granular –** ASTM sieve set**.**

Analytical and Testing Methods

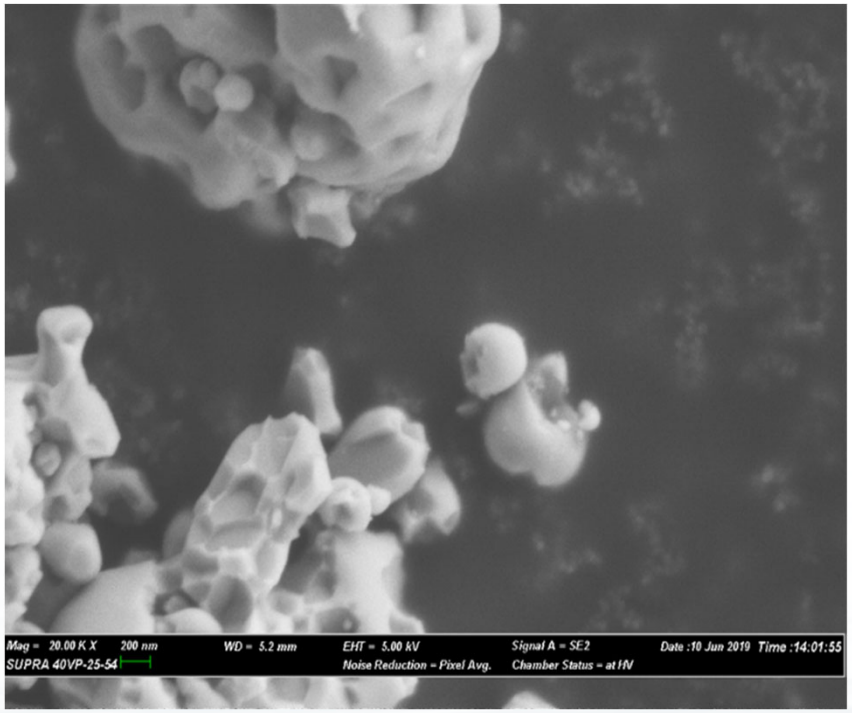
Zirconium Characterization (con't)

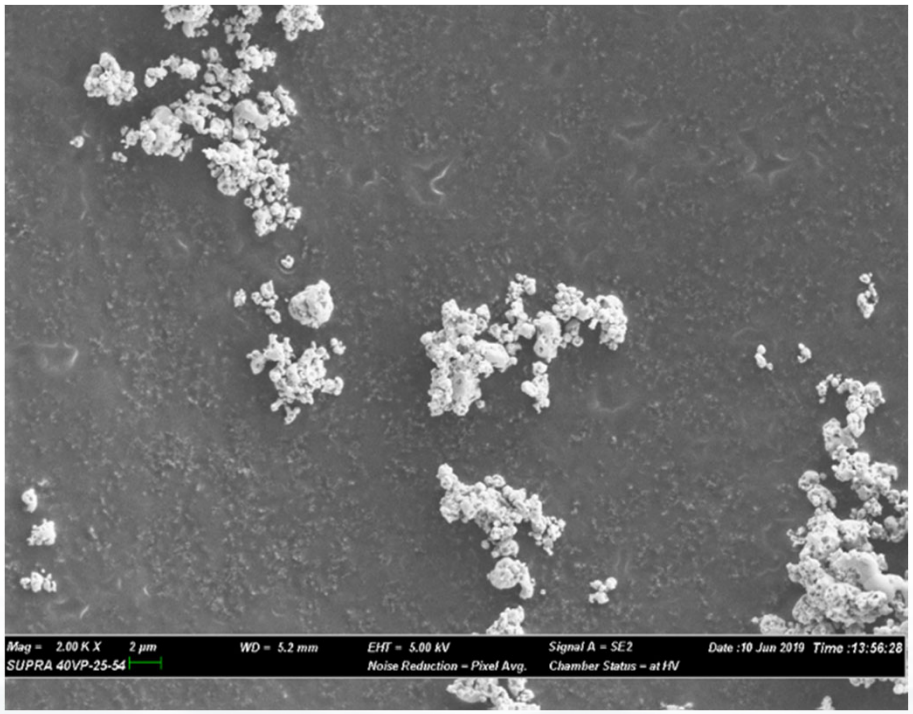
7. **Total Zr** – It was decided to use three different techniques to determine total Zr content Gravimetric Analysis, Thermogravimetric Analysis (TGA) – SDT Q600 TA Instruments, and chemical technique utilizing Inductively Coupled Plasma (ICP) technique. MIL-Z-399D requires determination by a traditional chemical method but Albemarle Co. recommends calculation of total Zr from ignition gain. This approach is questionable because the result is incorrect due to the presence of hafnium. Therefore, this approach as well as TGA provides combined Zr and Hf content. Therefore, IMP relied on ICP analyses and this technique has shown lower levels of Zr content, as expected.

8. **Ignition Gain** – Gravimetric gain (procedure from MIL-Z-399D) and TGA

9. **Burning Time** – Open Tray Method (procedure from MIL-Z-399D). Albemarle is using closed train method, but MIL-Z-399D refers to open train method. There are no technical specifications listed for the Albemarle technique.

Analyses of Zr Powders Purchased from Chemadyne Company (Type II Class 1)

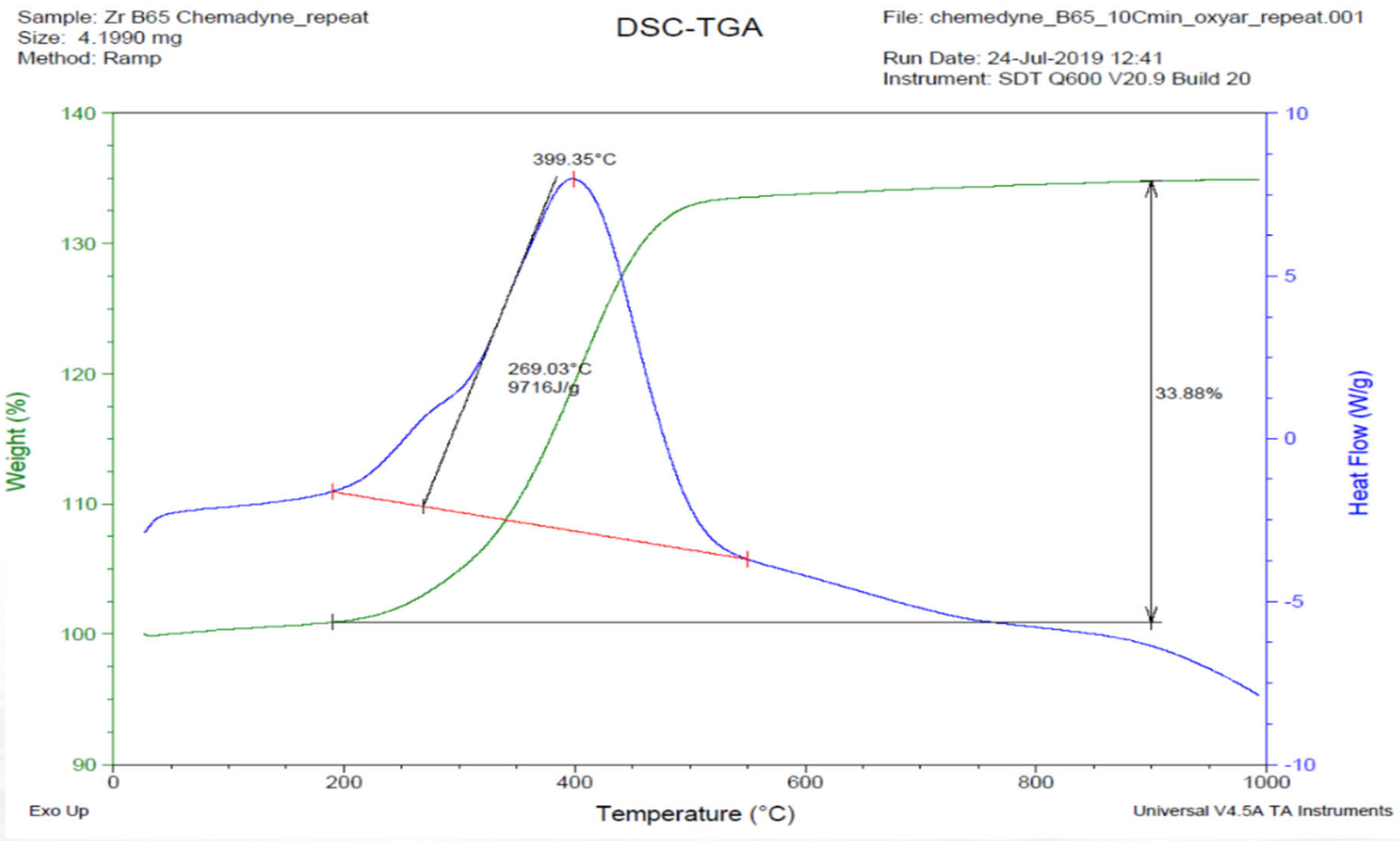




SEM photographs of Zr Type II Class 1 powder (Batch No. ZR21W_U22 Bottle 65) purchased from Chemadyne Company.

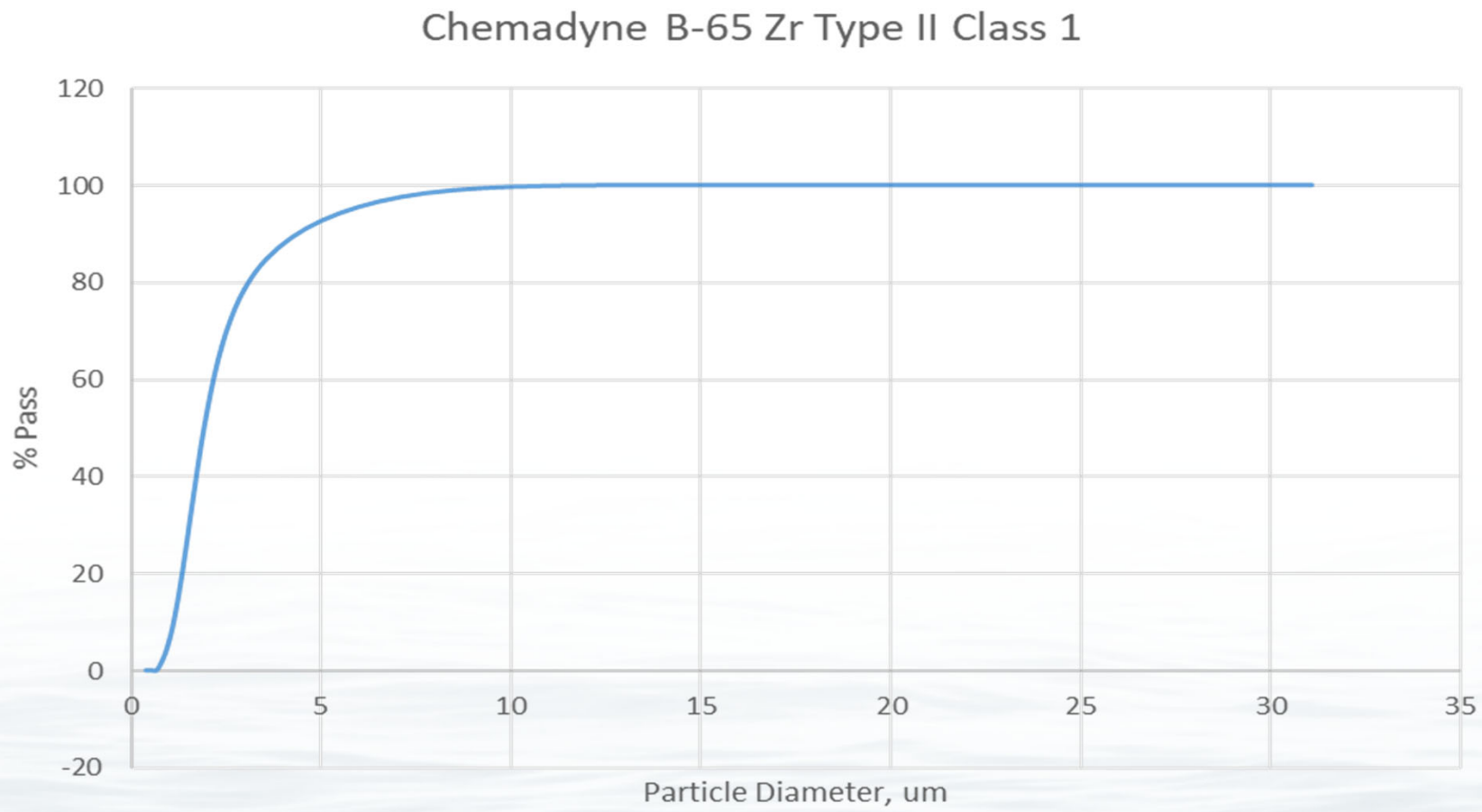
Photo Credits: Innovative Materials and Processes

Analyses of Zr Powders Purchased from Chemadyne Company (Type II Class 1)



TGA and DSC analysis of Zr Type II Class 1 powder (Batch No.ZR21W_U22 bottle B65) purchased from Chemadyne Company. Gas atmosphere: Ar/20%O_2.

Analyses of Zr Powders Purchased from Chemadyne (Type II Class 1)



Particle size analysis of Zr Type II Class 1 powder (Batch No. ZR21W_U22 bottle B65) purchased from Chemadyne Company. D_{MV} = 3.45 µm.

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Analyses of Zr Powders Purchased from Chemadyne (Type II Class 1)

Fraction	% Pass Analysis	% Pass MIL-Z399D
Thru 120 sieve (125 µm) by weight	100	100
Thru 200 sieve (74 µm)) by weight	100	99 min
Thru B.M. #26 sieve (20 µm)) by weight	100	96 min
Less than 9 µm by weight	99	85 min
3 µm percent by weight	77.5	70-90
0.75 µm percent by weight	1	12-30
Avg. particle size, microns	3.45	2.5±1

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Comparison of MIL-Z-399D requirements, vendor certificate of analysis listed in column 4, and IMP evaluation data for Zr Type II Class 1 powder (Batch No. ZR21W_U22 bottle B65) purchased from Chemadyne

Characteristics	MIL-Z-399D Type II, Class 1	MIL-Z-399D Type II, Class 1 Test Procedures	Chemadyne B65 Grade Zr Specification	Chemadyne Test Procedure	IMP Evaluation	IMP Test Procedure
Less than 125 µm	100%	sieving	Pass	n/a	100%	laser diffraction
Less than 74 µm	min. 99%	sieving	Pass	n/a	100%	laser diffraction
Less than 20 µm	min. 96%	sieving	Pass	n/a	100%	laser diffraction
Less than 45 µm	n/a	n/a	n/a	n/a	100%	laser diffraction
Avg. particle size	1.5 – 3.5 µm	FSSS	2.97 µm	n/a	3.45 µm	laser diffraction
Less than 9 µm	min. 85%	EP Turbimeter	Pass	n/a	99.0%	laser diffraction
Less than 3 µm	70 – 90%	EP Turbimeter	Pass	n/a	77.5%	laser diffraction
Less than 0.75 µm	12 – 30%	EP Turbimeter	Pass	n/a	1.0%	laser diffraction
Total Zr	min. 94%	chemically	96.7%	n/a	96.2%/94.8%	Calculated by ignition gain, TGA/from ignition gain in crucible
Zr	n/a	n/a	n/a	n/a	92.8%	ICP
Hf	n/a	n/a	n/a	n/a	0.861%	ICP
Ca	max. 0.10%	chemically	0.07%	n/a	0.0044%	ICP
Fe	max. 0.20%	chemically	0.09%	n/a	0.0259%	ICP
Al	max. 0.30%	chemically	0.19%	n/a	0.0135%	ICP
H	max. 0.20%	hot vacuum extraction	0.10%	n/a	0.1451%	hot vacuum extraction
Ignition gain	30.2 – 33.0%	gravimetric, gain in weight	31.10%	n/a	33.88%/28.05%	gravimetric, gain weight, TGA/ignition gain in crucible
BET	n/a	adsorption method	n/a	n/a	3.08 m^2/g	adsorption method
Burning time	1.3 – 2.4 s/10 inches open train burning	open train burning	2.1 s/10 inches	n/a	1.31 s/10 inches	open train burning

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Comparison of MIL-Z-399D requirements, vendor certificate of analysis listed in column 4, and IMP evaluation data for Zr Type II Class 2 powder (Batch No. ZR22W_U20-7 Bottle B52) purchased from Chemadyne.

Characteristics	MIL-Z-399D Type II, Class 2	MIL-Z-399D Type II, Class 2 Test Procedures	B-52 Grade Zr Specification	Chemadyne Test Procedure	IMP Evaluation	IMP Test Procedure
Less than 125 µm	100%	sieving	Pass	n/a	99.7%	laser diffraction
Less than 74 µm	min. 99%	sieving	Pass	n/a	99.67%	laser diffraction
Less than 20 µm	min. 96%	sieving	Pass	n/a	99.5%	laser diffraction
Less than 45 µm	n/a	n/a	n/a	n/a	99.4%	laser diffraction
Avg. particle size	1.7 – 2.3 µm	FSSS	2.21 µm	n/a	1.858 µm	laser diffraction
Less than 9 µm	min. 85%	EP Turbimeter	Pass	n/a	96.7%	laser diffraction
Less than 3 µm	70 – 90%	EP Turbimeter	Pass	n/a	77.5%	laser diffraction
Less than 0.75 µm	12 – 30%	EP Turbimeter	Pass	n/a	4.0%	laser diffraction
Total Zr	min. 95%	chemically	96.7%	n/a	89.7%/89.6%	Calculated by ignition gain, TGA/from ignition gain in crucible
Zr	n/a	n/a	n/a	n/a	94.5%	ICP
Hf	n/a	n/a	n/a	n/a	0.835%	ICP
Ca	max. 0.05%	chemically	0.01%	n/a	0.0046%	ICP
Fe	max. 0.03%	chemically	0.03%	n/a	0.0296%	ICP
Al	max. 0.15%	chemically	0.05%	n/a	0.0203%	ICP
H	max. 0.20%	hot vacuum extraction	0.17%	n/a	0.1778%	hot vacuum extraction
Ignition gain	30.2 – 33.0%	gravimetric, gain in weight	30.9%	n/a	31.48%/27.34%	gravimetric, gain weight, TGA/ignition gain in crucible
BET	n/a	adsorption method	n/a	n/a	2.25 m^2/g	adsorption method
Burning time	1.3 – 2.4 s/10 inches open train burning	open train burning	8 – 18 s/50 cm closed train method	n/a	1.28 s/10 inches	open train burning

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Comparison of MIL-Z-399D requirements, vendor certificate of analysis listed in column 4, and IMP evaluation data for Zr Type II Class 1 powder (Batch No. 2101005342) purchased from Albemarle.

Characteristics	MIL-Z-399D Type II, Class 1	MIL-Z-399D Type II, Class 1 Test Procedures	AB Grade Zr Specification	Albemarle Test Procedure	IMP Evaluation	IMP Test Procedure
Less than 125 µm	100%	sieving	100%	laser diffraction	100%	laser diffraction
Less than 74 µm	min. 99%	sieving	100%	laser diffraction	100%	laser diffraction
Less than 20 µm	min. 96%	sieving	100%	laser diffraction	100%	laser diffraction
Less than 45 µm	n/a	n/a	min. 99.9%	sieving	100%	laser diffraction
Avg. particle size	1.5 – 3.5 µm	FSSS	1.5 – 2.3 µm	Blaine	2.83 µm	laser diffraction
Less than 9 µm	min. 85%	EP Turbimeter	100%	laser diffraction	99.6%	laser diffraction
Less than 3 µm	70 – 90%	EP Turbimeter	70 – 90%	laser diffraction	82%	laser diffraction
Less than 0.75 µm	12 – 30%	EP Turbimeter	5 – 15%	laser diffraction	0.75%	laser diffraction
Total Zr	min. 94%	chemically	95.0 – 96.9%	Calculated by ignition gain	82.9%/94.1%	Calculated by ignition gain, TGA/from ignition gain in crucible
Zr	n/a	n/a	n/a	n/a	93.3%	ICP
Hf	n/a	n/a	n/a	n/a	0.940%	ICP
Ca	max. 0.10%	chemically	max. 0.10%	ICP	0.0196%	ICP
Fe	max. 0.20%	chemically	max. 0.10%	ICP	0.0106%	ICP
Al	max. 0.30%	chemically	max. 0.10%	ICP	0.0092%	ICP
H	max. 0.20%	hot vacuum extraction	max. 0.20%	carrier gas hot extraction	0.045%	hot vacuum extraction
Ignition gain	30.2 – 33.0%	gravimetric, gain in weight	28.4 – 30.9 %	gravimetric, gain weight	29.07%/27.12%	gravimetric, gain weight, TGA/ignition gain in crucible
BET	n/a	adsorption method	n/a	n/a	2.61 m^2/g	adsorption method
Burning time	1.3 – 2.4 s/10 inches open train burning	open train burning	5 – 20 s/50 cm closed train method	closed train burning	2.22 s/10 inches	open train burning

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Comparison of MIL-Z-399D requirements, vendor certificate of analysis listed in column 4, and IMP evaluation data for Zr Type II Class 2 powder (Batch No. 0000087558) purchased from Albemarle.

Characteristics	MIL-Z-399D Type II, Class 2	MIL-Z-399D Type II, Class 2 Test Procedures	CA Grade Zr Specification	Albemarle Test Procedure	IMP Evaluation	IMP Test Procedure
Less than 125 µm	100%	sieving	100%	laser diffraction	100%	laser diffraction
Less than 74 µm	min. 99%	sieving	100%	laser diffraction	100%	laser diffraction
Less than 20 µm	min. 96%	sieving	100%	laser diffraction	100%	laser diffraction
Less than 45 µm	n/a	n/a	min. 99.9%	sieving	100%	laser diffraction
Avg. particle size	1.7 – 2.3 µm	FSSS	1.7 – 2.3 µm	Blaine	2.853 µm	laser diffraction
Less than 9 µm	min. 85%	EP Turbimeter	Min 80%	laser diffraction	99.6%	laser diffraction
Less than 3 µm	70 – 90%	EP Turbimeter	30 – 45%	laser diffraction	82%	laser diffraction
Less than 0.75 µm	12 – 30%	EP Turbimeter	6 – 15%	laser diffraction	0.8%	laser diffraction
Total Zr	min. 95%	chemically	96.6 – 98.2%	Calculated by ignition gain	100.0%/94.2@	Calculated by ignition gain, TGA/from ignition gain in crucible
Zr	n/a	n/a	n/a	n/a	95.5%	ICP
Hf	n/a	n/a	n/a	n/a	0.953%	ICP
Ca	max. 0.05%	chemically	max. 0.05%	ICP	0.0047%	ICP
Fe	max. 0.03%	chemically	max. 0.07%	ICP	0.0082%	ICP
Al	max. 0.15%	chemically	max. 0.10%	ICP	0.0052%	ICP
H	max. 0.20%	hot vacuum extraction	max. 0.20%	carrier gas hot extraction	0.122%	hot vacuum extraction
Ignition gain	30.2 – 33.0%	gravimetric, gain in weight	30.5 – 32.5 %	gravimetric, gain weight	35.22%/26.50%	gravimetric, gain weight, TGA/ignition gain in crucible
BET	n/a	adsorption method	n/a	n/a	2.96 m^2/g	adsorption method
Burning time	1.3 – 2.4 s/10 inches open train burning	open train burning	8 – 18 s/50 cm closed train method	closed train burning	2.00 s/10 inches	open train burning

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Comparison of MIL-Z-399D requirements, vendor certificate of analysis listed in column 4, and IMP evaluation data for Zr Type I Class 2 granular (Batch No. ZR12W_33_1024 Bottle B4 purchased from Chemadyne

Characteristics	MIL-Z-399D Type I, Class 2	MIL-Z-399D Type I, Class 2 Test Procedures	B-4 Grade Zr Specification	Chemadyne Test Procedure	IMP Evaluation	IMP Test Procedure
Less than 177 µm	100%	sieving	Pass	n/a	100%/99.82%	laser diffraction/sieving
Less than 149 µm	min. 98%	sieving	Pass	n/a	99.96%/98.62%	laser diffraction/sieving
Less than 74 µm	max. 50%	sieving	Pass	n/a	67.15%/77.78%	laser diffraction/sieving
Less than 44 µm	max. 25%	n/a	Pass	n/a	25.92%/29.35%	laser diffraction/sieving
Less than 10 µm	max. 2%	EP Turbimeter	Pass	n/a	0.0%	laser diffraction
Total Zr	min. 96%	chemically	97.1%	n/a	86.9%/93.7%	Calculated by ignition gain, TGA/from ignition gain in crucible
Zr	n/a	n/a	n/a	n/a	88.9%	ICP
Hf	n/a	n/a	n/a	n/a	1.110%	ICP
Ca	max. 0.05%	chemically	0.04%	n/a	0.0119%	ICP
Fe	max. 0.30%	chemically	0.025%	n/a	0.164%	ICP
Al	max. 0.10%	chemically	0.07%	n/a	0.0737%	ICP
Cl	max. 0.03%	chemically	0.03%	n/a	0.0092%	ICP
Si	max. 0.10%	chemically	0.08%	n/a	0.372%, 0.531%	ICP
Sn	max. 0.75%	chemically	0.50%	n/a	0.0256%	ICP
H	max. 0.20%	hot vacuum extraction	0.15%	n/a	0.1056%%	hot vacuum extraction
Ignition gain	n/a	gravimetric, gain in weight	n/a	n/a	30.48%/26.50%	gravimetric, gain weight: TGA/combustion
BET	n/a	adsorption method	n/a	n/a	1.49 m^2/g	adsorption method

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Ignition gain determined by MIL-Z-399D and TGA

Zr Powder	Ignition gain in a ceramic crucible (air)	Ignition gain using TGA Ar-20 vol% O_2
Zr Type II Class 1 powder (Batch No. ZR21W_U22 bottle B65) purchased from Chemadyne	28.41% 27.68% 28.05% (avg)	33.88%
Zr Type II Class 2 powder Batch No. ZR22W_U20-7 Bottle B52 purchased from Chemadyne	28.63% 26.04% 27.34% (avg)	31.48%
Zr Type II Class 1 AB powder (Batch No. 2101005342) purchased from Albemarle Company.	27.78% 26.46% 27.12% (avg)	29.07%
Zr Type II Class 2 CA powder (Batch No. 0000087558) purchased from Albemarle Company.	28.50% 26.11% 27.31% (avg)	35.22%
Zr Type I Class 2 powder (Batch No. ZR12W_33_1024 Bottle B4 purchased from Chemadyne Company.	27.78% 25.22% 26.50% (avg)	30.48%

Total Zr determined from ignition gain during the combustion in crucible, TGA, and ICP

Zr Powder	From ignition gain in a crucible (air)	From TGA (argon-20 vol% O_2)	From ICP analysis
Zr Type II Class 1 powder (Batch No. ZR21W_U22 bottle B65) purchased from Chemadyne	94.8%	96.2%	92.8%
Zr Type II Class 2 powder Batch No. ZR22W_U20-7 Bottle B52 purchased from Chemadyne	89.6%	89.7%	94.5%
Zr Type II Class 1 AB powder ((Batch No. 2101005342) purchased from Albemarle Company.	94.1%	82.9%	93.3%
Zr Type II Class 2 CA powder (Batch No. 0000087558) purchased from Albemarle Company.	94.2%	100%	95.5%
Zr Type I Class 2 powder (Batch No. ZR12W_33_1024 Bottle B4 purchased from Chemadyne Company.	93.7%	86.9%	88.9%

Conclusions and Recommendations

- All five Zr powders from two companies: i) Chemadyne (Type I Class 2, Type II Class 1, and Type II Class 2) and ii) Albemarle (Type II Class 1 and Type II Class 2) were extensively evaluated. It was concluded that not all MIL-Z-399D were exactly met by the manufacturers.

- The determination of hydrogen content by vacuum extraction technique is adequate. However, it was concluded that the instrumentation for this technique is not widely available and other analytical methods based on fusion extraction into an inert gas and analysis by a high sensitivity thermal conductivity detector might be more convenient, due to the wide availability of such analytical equipment. Therefore, further tests are recommended using this equipment.

- It should be also noted that some MIL-Z-399D measurement techniques are quite outdated and more modern and more accurate techniques should be recommended. Some tests, e.g. ignition gain, should have more precision. The temperature of roasting Zr powder should be specified – e.g., min 800^{o}C in order to complete oxidation of Zr to ZrO_2.

- Based on a literature review, it was concluded that Hf content determination along with other elements required by the Mil-Z-399 could be more efficiently and precisely determined by ICP technique.