ORNL/TM-2023/2896

Characterization of Aluminum Metal Powders for Plutonium-238 Program

Kathryn M. Peruski
Chris L. Jensen
Samantha K. Cary

May 2023

OAK RIDGE National Laboratory

ORNL IS MANAGED BY UT-BATTELLE LLC FOR THE US DEPARTMENT OF ENERGY

ORNL/TM-2023/2896

Nuclear Energy and Fuel Cycle Division

CHARACTERIZATION OF ALUMNIUM METAL POWDERS FOR PLUTONIUM-238 PROGRAM

Kathryn M. Peruski
Chris L. Jensen
Samantha K. Cary

May 2023

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831
managed by
UT-BATTELLE LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

FIGURES

TABLES

1. INTRODUCTION

As part of radioisotope thermoelectric generator (RTG) production for power sources in deep space exploration, Oak Ridge National Laboratory (ORNL) produces plutonium-238 (^{238}Pu). To produce ^{238}Pu, neptunium-237 (^{237}Np) targets are fabricated at ORNL and subsequently irradiated at the High Flux Isotope Reactor (HFIR) at ORNL and the Advanced Test Reactor (ATR) at Idaho National Laboratory (INL). Specifically, current flowsheets utilize neptunium dioxide ($^{237}NpO_2$) targets. Aluminum (Al) powder is blended with $^{237}NpO_2$ target material to improve thermal conductivity during irradiation. The current composition of $^{237}NpO_2$/Al pellets (i.e., cermets, or ceramic–metallics) is 20% $^{237}NpO_2$, 70% Al, and 10% void space [1].

Al powders utilized by the ^{238}Pu program are high-fired under vacuum before blending into targets. The primary objective of this work is to measure the physical, chemical, and thermal properties of Al before and after the high-firing process. Properties of interest include the morphology, surface texture, particle size, crystal phase(s), and thermal conductivity of the material. These properties are measured with existing materials characterization equipment at ORNL, including powder x-ray diffraction (pXRD), scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS), laser flash analysis (LFA), and thermogravimetric analysis (TGA). A secondary objective of this work is to compare the Al powders before and after the high-firing procedure to determine the effects of high-firing on chemical, physical, and thermal properties and to determine the efficacy of the high-firing process.

2. MATERIALS AND METHODS

Aluminum powders are characterized using four different analytical techniques: pXRD, SEM with EDS, LFA, and TGA with on-line mass spectrometry. Aluminum powders are atomized, nodular aluminum powder grade 101 from Toyal America, Inc. with a manufacture date of 01/11/2019. Aluminum powder, as purchased, was sieved to below a 325-mesh size, which was verified by compliance analysis at the manufacturer. At ORNL, the Al powder is fired in a vacuum furnace at 500°C, with a 3 h ramp time and 4 h hold time. After high-firing, the Al is sieved and stored inside a desiccator.

2.1 POWDER X-RAY DIFFRACTION

As-received Al powders (pre-fire and high-fired) are analyzed by pXRD to determine crystal phase(s) present. Analysis is performed on a Malvern Panalytical Empyrean diffractometer with a scan range of 5–90 2θ and a step size of 0.013. After analysis, recorded pXRD patterns are compared with the standard patterns for Al metal and aluminum oxide (Al_2O_3) from the Inorganic Crystal Structure Database (ICSD) for phase determination.

2.2 SCANNING ELECTRON MICROSCOPY

As-received Al powders (pre-fire and high-fired) are characterized using SEM equipped with EDS to probe surface morphology, particle size, and elemental composition at the surface. Samples are prepared by sprinkling dry powder onto double-sided carbon tape affixed to an Al SEM stub. Samples are not sputter coated. SEM analysis is performed on a Hitachi S4700 field-emission SEM, equipped with Oxford Aztec Microanalysis EDS system. Data are collected at a working distance of 8.0 mm for imaging and a working distance of 12.0 mm for elemental analysis, with a consistent accelerating voltage of 15.0 kV and current of 10 uA for all analyses. Micrographs are not post-processed or altered in any manner.

2.3 LASER FLASH ANALYSIS

The thermal diffusivity of the Al is measured using a LFA system, which can be used to determine thermal conductivity assuming a known specific heat and density of the material of interest. As-received Al powder is pressed into pellets for LFA using a single-axis hydraulic Carver press with a ¼ in. diameter die. Physical characteristics, including the weight, diameter, and height of each pellet, are recorded and utilized to calculate pellet density. Pellet characteristics are provided in Table 1.

Table 1. Physical characteristics of pressed Al pellets

Sample ID	Press Pressure (lbs)	Pellet Mass (g)	Pellet Height (cm)	Pellet Diameter (cm)	Pellet Density (g/cm^3)
UnfiredAl_1	5400	0.176	0.230	0.62992	2.4626
UnfiredAl_2	5400	0.175	0.210	0.62992	2.67398
FiredAl_1	5400	0.175	0.207	0.62992	2.71273
FiredAl_2	5400	0.1741	0.215	0.62992	2.598362
FiredAl_3	5400	0.134	0.16002	0.62992	2.6899
FiredAl_4	5400	0.156	0.18669	0.62992	2.68157

LFA for thermal conductivity determination is performed on a Netzsch LFA 447 Nanoflash, equipped with a Xe flash lamp and liquid nitrogen–cooled InSB infrared detector. A detailed report on the operation and capabilities of this instrument in relation to Al and cermet measurements is provided in a previous report by Toney and Jensen [2]. To briefly describe methods: pellet samples are coated with graphite spray prior to analysis for enhanced energy absorption and emission. Measurements are performed at operating temperatures of 50, 100, 150, 200, and 250°C with one measurement per temperature step and a 1 min delay between measurements. Thermal conductivity is calculated as a function of measured thermal diffusivity:

$$\lambda = \alpha \times \rho \times C_p \, ,$$

where λ is thermal conductivity, α is thermal diffusivity, ρ is density, and C_p is specific heat capacity. For conversion of the measured thermal diffusivity to thermal conductivity, the known physical parameters of each pellet (thickness and density) and the reference value for Al specific heat (0.9229 J/g °C) are input for each measurement. Subsequently, data are modeled using the Cowan + pulse correction model in the Netzsch Proteus LFA Analysis module using all measured and input data. All LFA data are reported as calculated thermal conductivity values.

2.4 THERMOGRAVIMETRIC ANALYSIS

Pre-fire Al powder is analyzed using TGA with a coupled mass spectrometer to determine whether the unfired Al powder underwent hydration during storage and to determine whether any change to the Al powder occurred during the firing process. A 10 mg sample of pre-fire Al powder is placed in an 85 µL alumina crucible with lid for analysis. Analysis is performed on a Netzsch Simultaneous Thermal Analyzer (Model 449 F1 Jupiter), which has a 25 ng mass resolution, equipped with a silicon carbide furnace. The STA is also equipped with an Aeolos quadrupole mass spectrometer (QMS) for determination of constituents in the off-gas from the sample. The Al sample is equilibrated under vacuum with an ultra-high–purity Ar gas (UHP Ar) purge and measured to 300°C at a ramp speed of 10°C/min. QMS monitoring is set for m/z=18 to determine the release of water from the sample.

3. RESULTS AND DISCUSSION

3.1 POWDER X-RAY DIFFRACTION

Powder XRD analysis of the pre-fire and high-fired Al powders shows the presence of Al metal as the bulk crystal phase. The pre-fire Al sample has a pXRD pattern that aligns well with the known peaks for Al metal and does not match with aluminum oxide peaks (Figure 1). The recorded diffraction pattern indicates that the bulk material is Al metal. However, the limit of detection (LOD) for pXRD is approximately 5 wt %, meaning that there could be trace-level impurities that are not detectable via this analysis.

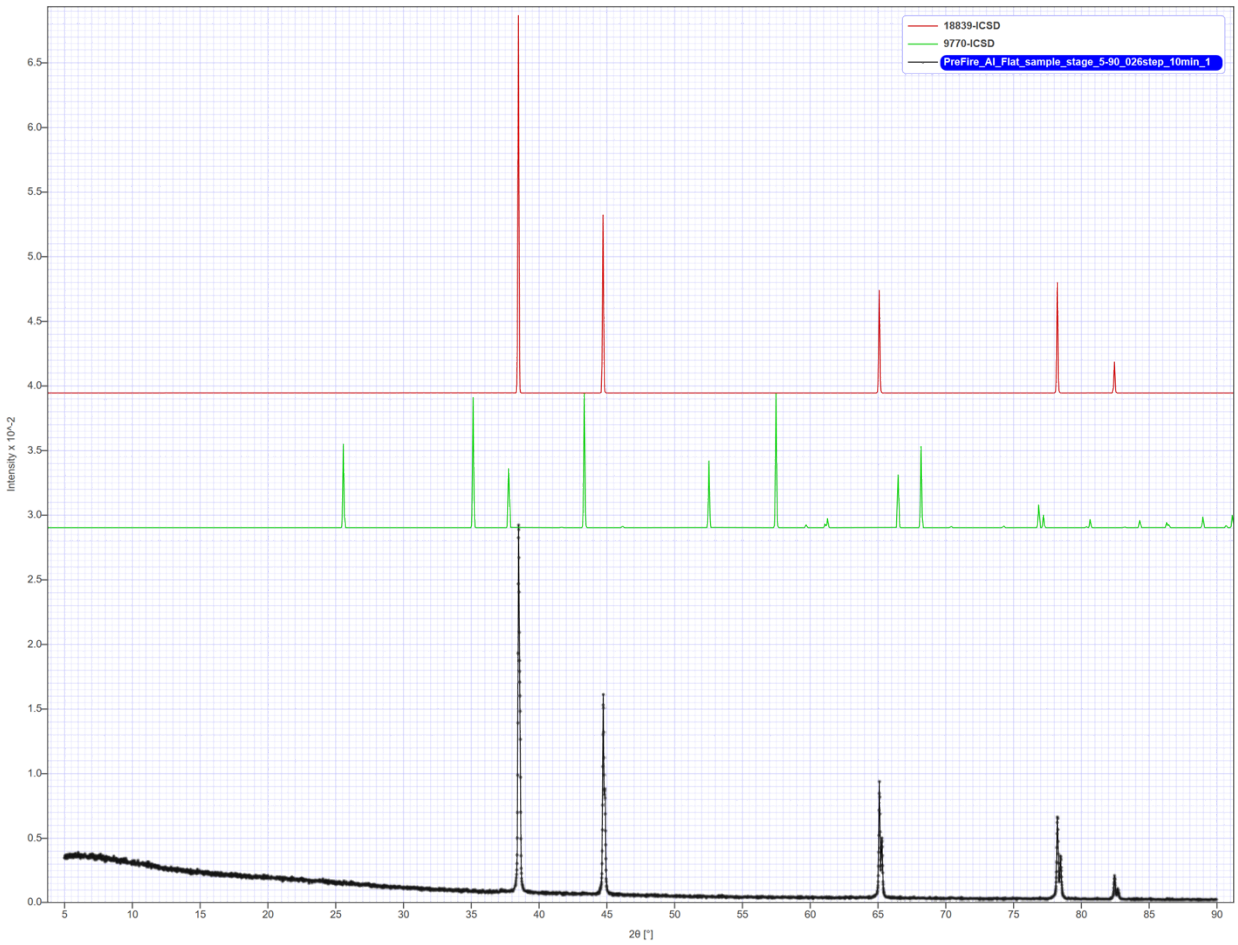

Figure 1. Powder X-ray diffraction pattern of pre-fire aluminum (black trace), aluminum oxide standard (green trace), and aluminum metal standard (red trace).

Like the pre-fire Al, the high-fired Al pXRD pattern indicates the presence of Al metal in the bulk material. Comparing the collected data from the top cap Al to the standard reference patterns of Al and aluminum oxide, the peaks align closely with Al metal and do not align with aluminum oxide (Figure 2). As previously stated, this analysis may not account for trace (<5 wt %) impurities. However, the pXRD analysis of both pre-fire and high-fired Al indicate that the bulk material is Al metal. Additionally, the pre-fire and high-fired Al pXRD patterns are identical, indicating no bulk phase changes during the firing process.

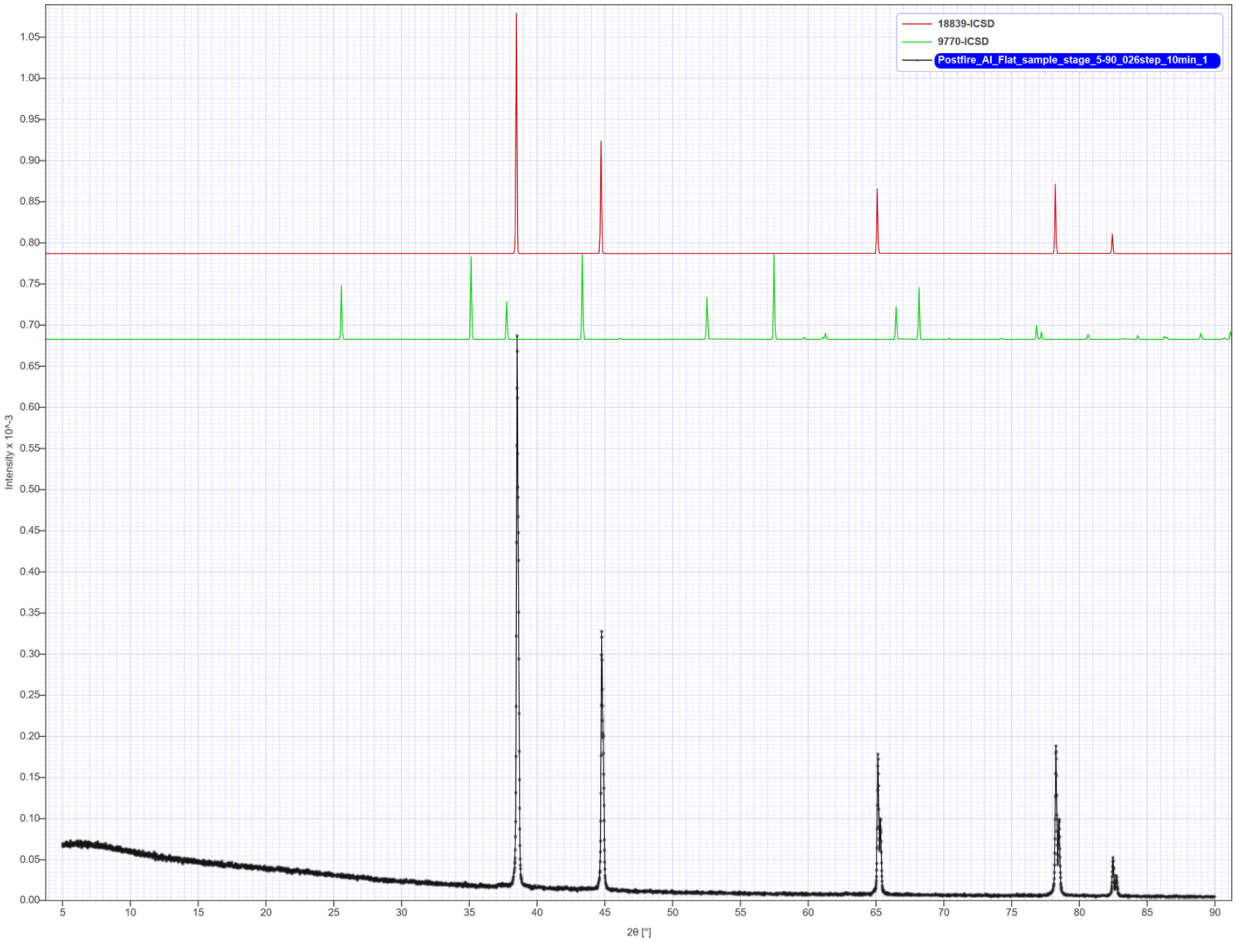

Figure 2. Powder XRD pattern of high-fired aluminum (black trace), aluminum oxide standard (green trace), and aluminum metal standard (red trace).

3.2 SCANNING ELECTRON MICROSCOPY

Micrographs of the pre-fire and high-fired Al exhibit significant heterogeneity in aggregate size and morphology. However, no clear differences were identified in morphology or size before and after firing in the physical characteristics of the samples. The pre-fire Al powder contains large aggregates, approximately 5–50+ µm in length (Figure 3). Higher magnification micrographs of these aggregates show that the aggregates are composed of primary particles that are slightly angular to rounded in morphology and 1–5 µm in diameter (Figure 4).

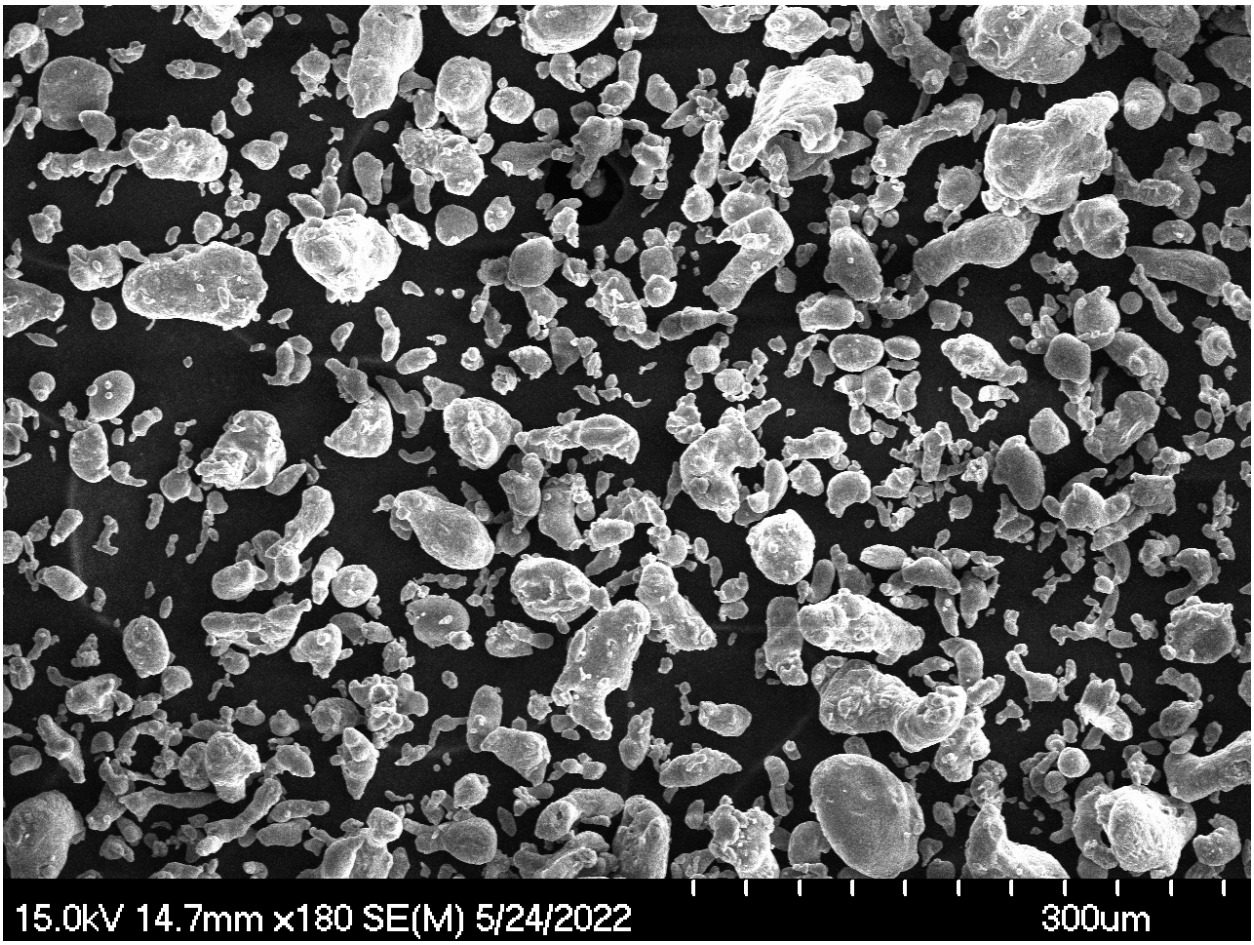

Figure 3. Micrograph of pre-fire Al powder.

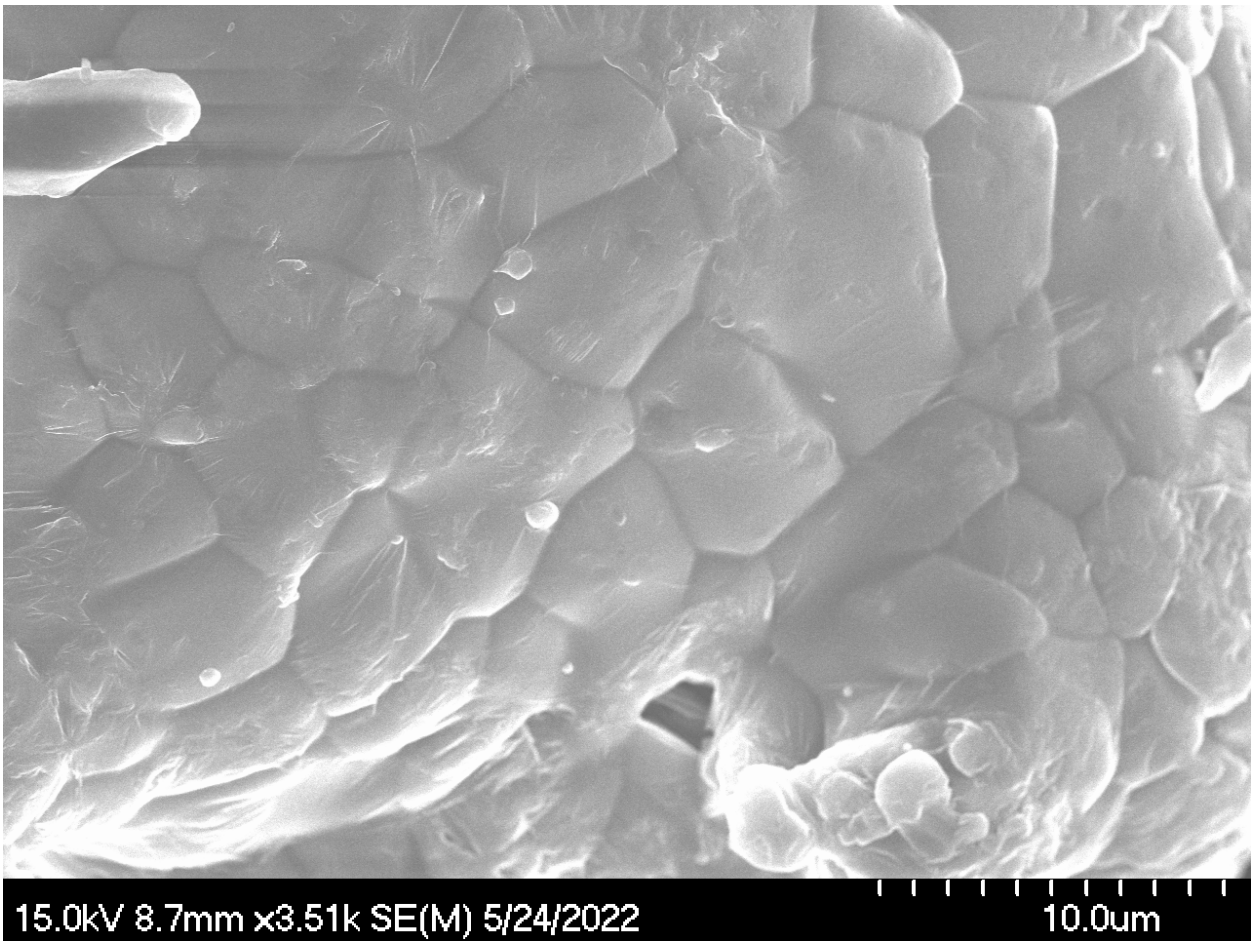

Figure 4. High-magnification micrograph of pre-fire Al powder.

Like the pre-fire Al, the high-fired Al also contains heterogenous aggregated particles. Micrographs show aggregated particles that are 5–50 μm in length (Figure 5). The primary particles that make up the aggregate are also smaller than 1–5 μm in diameter with slightly angular to rounded morphologies (Figure 6).

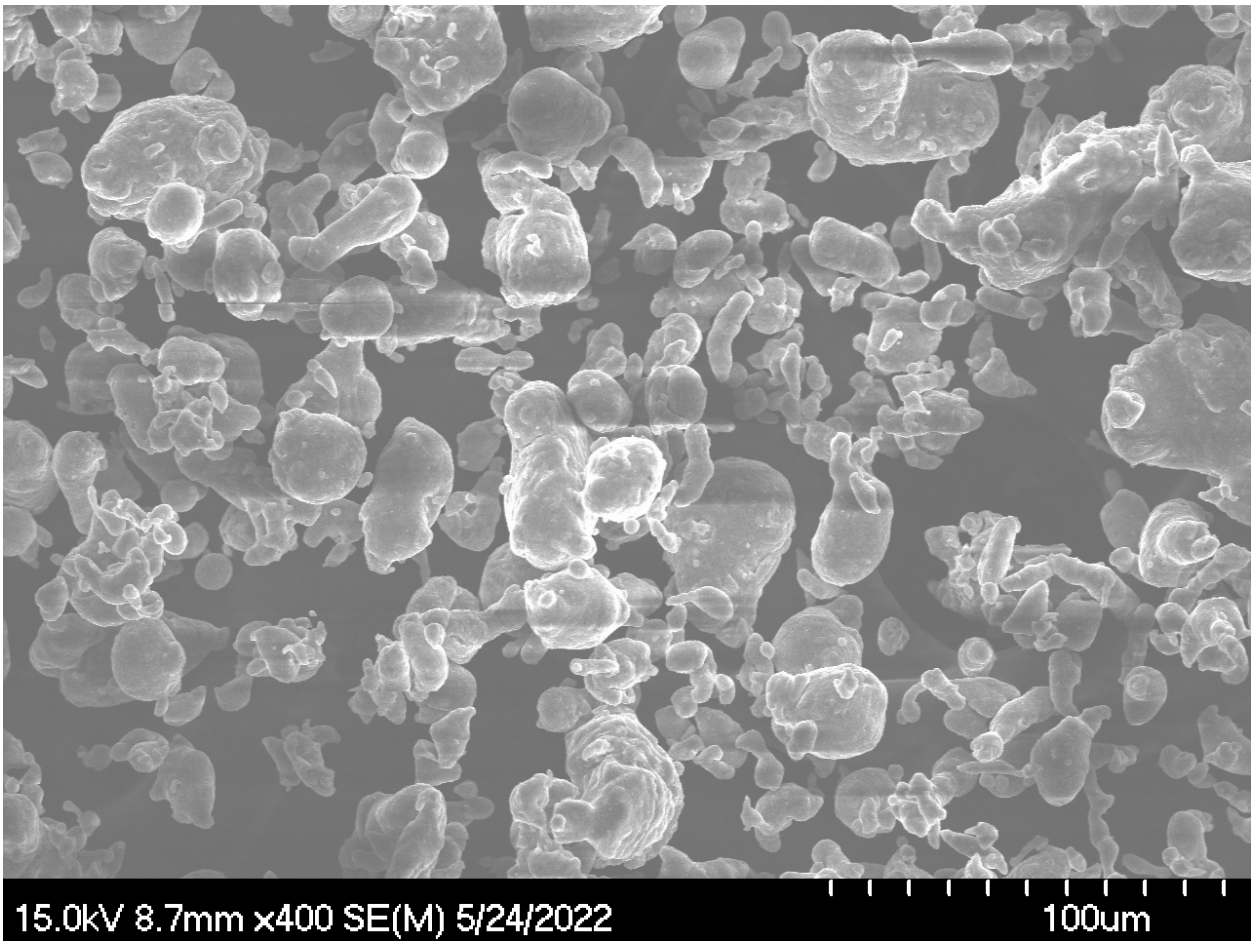

Figure 5. Micrograph of high-fired Al powder.

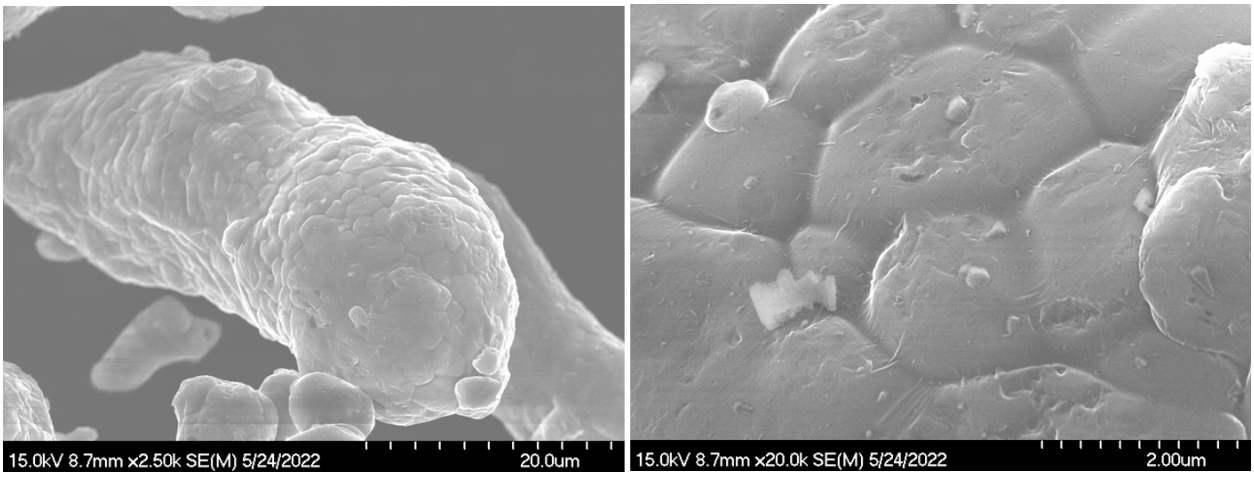

Figure 6. High-magnification micrographs of high-fired Al.

Overall, SEM analysis showed no clear difference in the morphology and particle size of pre-fire and high-fired Al samples as observed by SEM analysis. The micrographs in Figures 3–6 are nearly indistinguishable. It is important to note that significant heterogeneity in the size and shape of aggregates exists within each sample. Much of the powder is “fines,” with aggregate sizes on the order of tens of

microns. This heterogeneity in aggregate size is best visualized in low-magnification micrographs (Figure 3 and Figure 5).

Elemental analysis of the surface of the pre-fire and high-fire Al via EDS shows little difference in elemental composition between the two preparations and little indication of chemical impurity of the Al powder. For the pre-fire Al, Al is the only element detected on the surface of the sample (Figure 7). This measurement is of the elemental composition of the *surface* of the sample. Unlike pXRD, which is a bulk measurement of composition of the sample and has a limit of detection (LOD) of approximately 5 wt %, EDS analyzes the composition of the surface layers of a material at trace levels. These two techniques are complementary for complete understanding of a material's chemical composition at both bulk and trace levels.

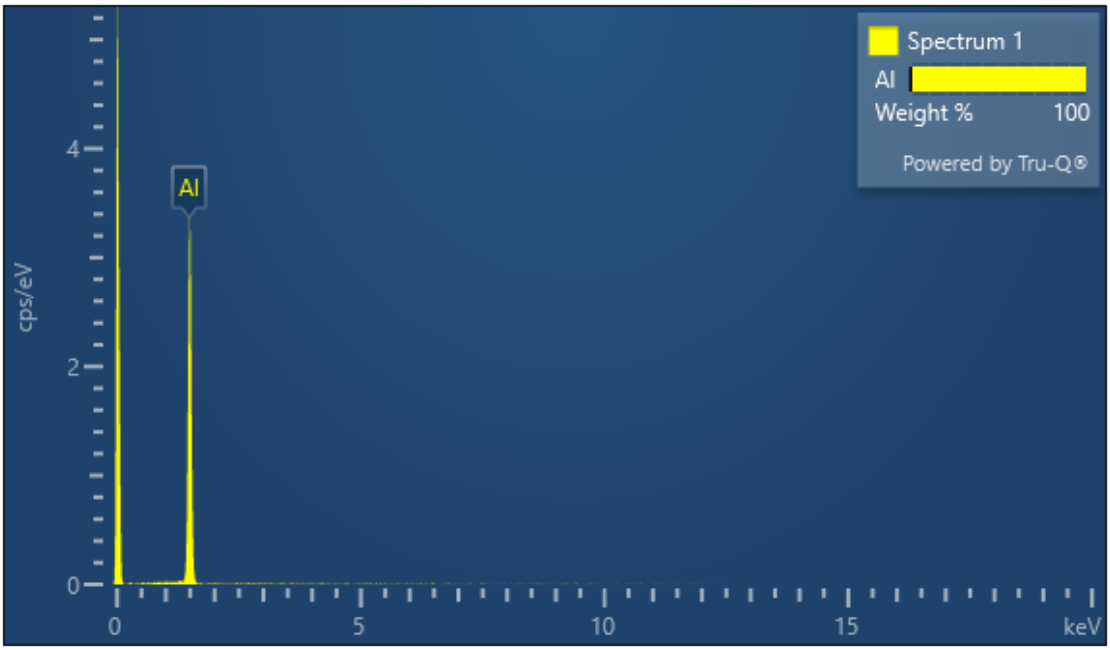

Figure 7. EDS spectrum of pre-fire Al.

The high-fired Al shows trace oxygen at the surface of the sample, the majority of the surface remaining as Al. EDS detects approximately 2.5 wt % oxygen at the surface of the high-fired Al sample with 97.5% Al (Figure 8). The origin of this impurity is not clear and may be the result of sample storage or the high-firing process itself.

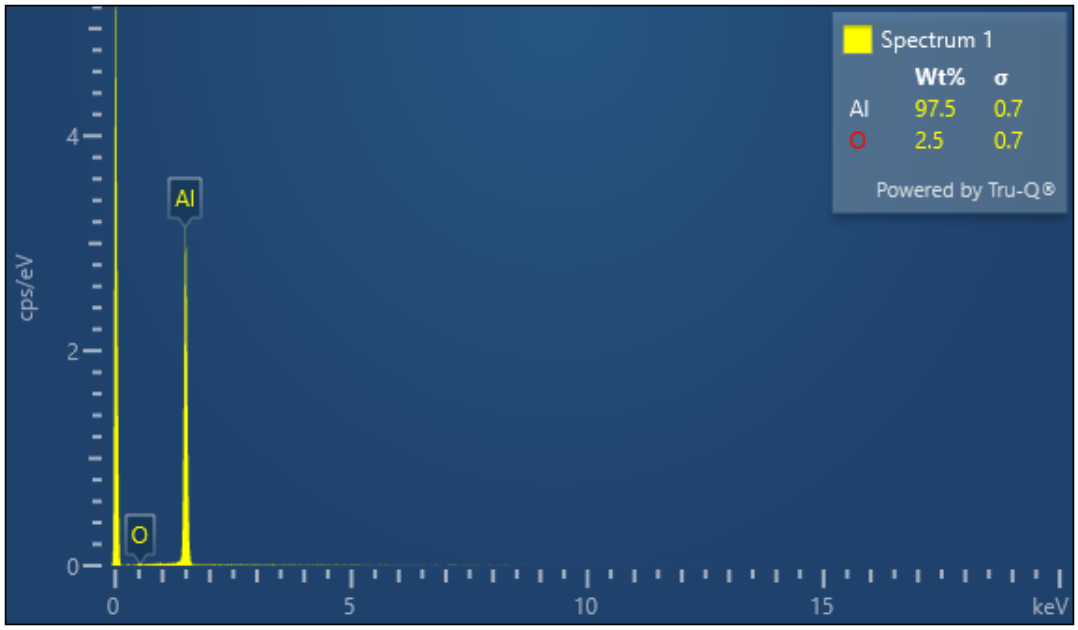

Figure 8. EDS spectrum of high-fired Al.

3.3 LASER FLASH ANALYSIS

LFA of pressed Al pellets (Table 1) is used to determine the thermal conductivity of the Al at temperatures in the 50–250°C range. Calculated thermal conductivity values range from 60 W/m·K to 184 W/m·K, depending on measurement temperature and pellet (Table 2).

Table 2. Calculated thermal conductivity values for core Al pellets

Sample ID	Thermal Conductivity (W/m·K) @ 50°C	Thermal Conductivity (W/m·K) @ 100°C	Thermal Conductivity (W/m·K) @ 150°C	Thermal Conductivity (W/m·K) @ 200°C	Thermal Conductivity (W/m·K) @ 250°C
UnfiredAl_1	184.621	180.948	178.559	172.733	172.033
UnfiredAl_2	128.598	125.901	124.678	122.443	119.119
FiredAl_1	113.125	111.722	109.313	107.749	106.072
FiredAl_2	66.188	63.460	61.604	60.613	60.167
FiredAl_3	143.22	140.026	137.327	134.467	129.624
FiredAl_4	153.223	149.318	144.627	142.444	138.279

Literature values for the thermal conductivity of Al and Al alloys vary significantly, especially based on temperature and the alloy. There are no reported reference values for pressed pellets of Al powders with which to compare against the measured values. However, well-annealed high-purity solid Al is reported to have thermal conductivities in the 236–240 W/m·K range and temperatures ranging from 25°C to 227°C [3, 4]. An alternate report from the American Society of Metals (ASM) Handbook (Vol. 15) reports that pure Al has thermal conductivity values ranging from 91 W/m·K to 211 W/m·K [5] and that Al alloys can be in the range of 100–210 W/m·K [5], with measurements at low temperatures. The measured thermal conductivities of the Al pellets tested here are within reported ranges for reference Al.

The measured thermal conductivities for the non-fired Al are, on average, higher than the measured thermal conductivities for the high-fired Al (Table 2). However, a large range of thermal conductivity values is observed for the high-fired Al as well as noticeable variation in the data. The comparable, or higher, thermal conductivities of the unfired Al suggest that the high-firing process does not improve the thermal conductivity of the Al powder used in cermet fabrication.

3.4 THERMOGRAVIMETRIC ANALYSIS

TGA and mass spectrometry of evolved gas are used to determine whether the Al powders used in target fabrication contain any residual water due to storage conditions. During heating in an Ar(g) atmosphere, the unfired (raw) Al powder showed no mass change (Figure 9). Additionally, over the same time and temperature range, the mass spectrometer recorded no increase in nor the presence of any water (m = 18) (Figure 9). These two pieces of data in combination suggest that the Al contains no residual water that can be removed by firing the material. Overall, the TGA data indicate no change in the Al mass or chemical composition during the firing process.

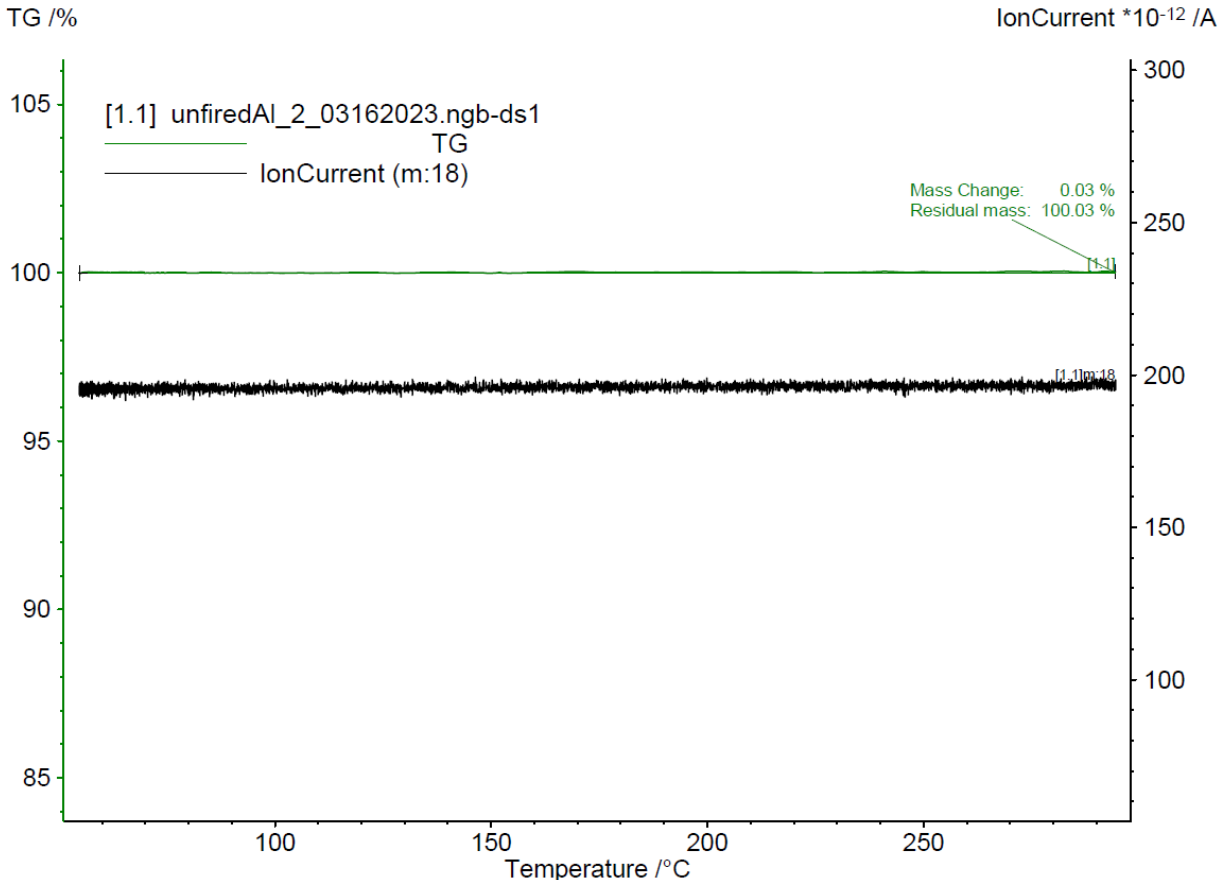

Figure 9. Recorded mass (relative) of Al powder (green trace) and mass spectra (m = 18) (black trace) over temperature range of 60–300°C from TGA-MS analysis of unfired Al.

4. CONCLUSIONS

Al powders utilized by the ^{238}Pu were analyzed using solid-state characterization techniques, including pXRD, SEM-EDS, LFA, and TGA. The primary objective of this work was to measure and compare the physical, chemical, and thermal properties of Al before and after the high-firing process. pXRD data showed pure Al metal as the bulk crystal phase present in both pre-fire and high-fired Al, with no reportable changes in the bulk material due to the firing process and no evidence of oxide phases. Furthermore, SEM-EDS data confirmed that there were no physical or chemical changes to the Al metal during the firing process, with consistent morphology, particle size, and elemental composition in both Al samples. A key concern for chemical analysis was the potential for buildup of an aluminum oxide layer on the surface of the Al metal; however, no evidence of this phenomenon was observed in the SEM-EDS data. Additionally, measured thermal conductivity values of pressed Al pellets were higher in the pre-fire Al than after the high-firing process and in good agreement with literature references for Al metal thermal conductivity. Finally, TGA-MS indicated that Al metal powders have no residual water that can be liberated by firing the material. Overall, the results of work imply that the high-firing process for Al powder does not change, or improve, the physical or chemical characteristics of the Al powder.

5. REFERENCES

1. Collins, E. D.; Morris, R. N.; McDuffee, J. L.; Mulligan, P. L.; Delashmitt, J. S.; Sherman, S. R.; Vedder, R. J.; Wham, R. M., Plutonium-238 Production Program Results, Implications, and Projections from Irradiation and Examination of Initial NpO2 Test Targets for Improved Production. *Nuclear Technology* **2022**, 1-8.
2. Toney, G.; Jensen, C. *Technical Guidance on Use of the Netzsch LFA 447 Nanoflash for Measurement of Ceramic-Metallic (Cermet) Pellet Specimen*; Oak Ridge National Laboratory Oak Ridge, TN, 2022.
3. Powell, R.; Ho, C. Y.; Liley, P. E., *Thermal conductivity of selected materials*. US Department of Commerce, National Bureau of Standards Washington, D.C., 1966; Vol. 8.
4. Hatch, J. E., *Aluminum: properties and physical metallurgy*. ASM international: Metals Park, Ohio, 1984.
5. Valencia, J. J.; Quested, P. N., *Thermophysical properties*. ASM International: 2013; Vol. 15.