Fabrication, Classification, and Characterization of Tellurium Powders

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FABRICATION, CLASSIFICATION, AND CHARACTERIZATION
OF TELLURIUM POWDERS

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ABSTRACT

Tellurium powder is used as a constituent in heat-producing, thermite-type reactions. In such reactions, long-term stability and reaction rate considerations require a compromise between surface area and particle size. To meet these requirements, a spherical powder was fabricated by atomizing liquid tellurium. In general, air classification techniques proved to be the most successful means of removing adherent fines from tellurium powders. Development of a minimum set of standard powder characterization techniques is outlined and applied to several spherical and irregular tellurium powders.

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FABRICATION, CLASSIFICATION, AND CHARACTERIZATION OF TELLURIUM POWDERS

Introduction

Sandia Laboratories' interest in tellurium (Te) powder is as a constituent in explosive and thermite devices. In these devices, the reaction enthalpy during rapid alloying with a metal (like Co) produces an intense heat. However, two of the design criteria for such devices imply contrasting powder properties. To ensure rapid and complete alloying, a fine Te particle size is needed. On the other hand, the design requirement for long-term stability implies a small surface area (i. e., large particle size) to minimize interfacial reactions. The need for a balance between these contrasting Te powder characteristics led to a development effort devoted to assessing various approaches for Te powder fabrication, classification, and characterization. Although this presentation is not comprehensive, it does establish an initial basis for formulating material specifications for future studies.

Tellurium Powder Technology

Physical powder characteristics such as size and packing density have strong influences on thermite reaction rates, heat intensity, and overall system stability. Thus, to develop the relations between thermite reaction properties and powder characteristics is a desirable goal. Such a goal requires powder samples with known property variations, which, in turn, requires a suitable means of characterizing each powder sample. For this reason, considerable emphasis was placed on developing powder characterization techniques applicable to Te. Furthermore, quantitative evaluation of the various fabrication and classification approaches explored in this program relied on development of quantitative characterization techniques. The intent was not to create a comprehensive powder characterization schedule, but rather to establish the minimum set of measurements necessary to characterize each powder.

Powder Characterization

The important powder properties are the size distribution, particle shape, interparticle friction, and internal particle structure.¹ Obviously, the particle size is influential because chemical reactivity is inversely dependent on the particle diameter (i. e., directly dependent on the specific surface area). For example, the Kelvin equation for vapor pressure and the Freundlich-Ostwald equation for solubility both exhibit the same particle size dependence:²

$$\ln(P/P_0) = \ln(C/C_0) = 2\gamma V/kTd \quad (1)$$

where P_0 = vapor pressure, P = vapor pressure over a curved surface, C = solubility, C_0 = solubility of the material without curvature, γ = surface energy, V = molar volume, k = Boltzmann's constant, T = temperature, and d = particle diameter (assumed spherical). Equation (1) illustrates the increased chemical activity which results from a reduced particle size. In a powder sample with a wide size distribution, the fines segment have the greatest influence on chemical reactivity. With respect to a thermite reaction, the specific surface area S is an ideal measure of the reactivity. The specific surface area relates to the mean particle diameter on a population basis ($\bar{d}_N$) as

$$S = \frac{6}{\rho \bar{d}_N} \quad (2)$$

where ρ = theoretical density (6.24 g/cm³ for Te). One aspect of the surface area important to the present study is that it is influenced mostly by the finer particles. If a weight distribution is known, the mean particle size $\bar{d}_W$ can be used to approximate $\bar{d}_N$ (and thereby calculate S from Equation (2)) as follows:^{3, 4}

$$\ln \bar{d}_W = \ln \bar{d}_N + 3 \ln^2 \sigma_g \quad (3)$$

where σ_g is the geometric standard deviation of the distribution. Thus a relative measure of chemical reactivity can be established by determining either the specific surface area or the particle size distribution. For this study, the specific surface area was measured routinely by nitrogen adsorption and supplemented with size distribution information whenever appropriate.

Besides the particle size, the particle shape is important in that a locally small radius of curvature (e. g., a sharp corner) can act to increase the chemical reactivity. That is, d in Equation (1) can actually be thought of as a radius of curvature. Also, the particle shape and size distribution control the powder-packing properties through the interparticle friction.

For thermite reactions, where large heat densities are sought, uniformly sized, dense, spherical particles will give better powder packing. Typically these friction properties can be qualitatively compared by microscopy or quantitatively assessed by the apparent and tap densities of the powder.⁵ Finally, the fourth important parameter is the internal structure. Generally, this structure is most appropriately analyzed by standard optical metallography techniques as applied to random cross sections through mounted and polished particles. Metallographic analysis will provide information on the internal porosity, grain structure, and degree of particle agglomeration.

It was found that scanning electron microscopy combined with nitrogen adsorption specific surface area proved adequate for an initial powder characterization. If interest in a powder warranted further effort, these techniques were supplemented with optical metallography and particle size analysis. A variety of techniques for particle size analysis^{6,7} were surveyed for their applicability to the Te powders. Table I summarizes these techniques and gives comments on their applicability. As shown, the relative toxicity of Te prevented some approaches properly suited to these powders from being pursued. Of these techniques, both the Zeiss and Coulter instruments proved adequate for determining the particle size distribution and were used on several powder lots during this study. Further details of the characterization techniques are given in Appendix A.

Powder Fabrication

Tellurium's brittle nature makes powder fabrication by attrition or pulverization quite easy. Such mechanical powder fabrication processes resulted in undesirable angular particles. In addition, these processes also generate a considerable amount of adherent fines during the comminuting of wrought Te. Figure 1a shows a scanning electron micrograph of a typical powder sample produced by attrition. Removal of the adherent fines proved to be a major problem with this powder, as will be discussed in the next section. The alternative powder production method commercially applied to Te is electrochemical precipitation. A typical precipitated powder is shown in Figure 1b. No consideration was given to this powder because of high impurity levels, amorphous nature, high reactivity, fine size, and poor packing characteristics.

The powder fabrication technique eventually developed in this program was based on inert gas atomization of liquid Te. The spherical shape of powders produced by this process is an attractive characteristic. Furthermore, spherical particles provide high packing densities and are easily classified into narrow size ranges by means of conventional equipment. The typical powder appearance following atomization is shown in Figure 2. It was found that the powder size distribution could be controlled by the atomization parameters. Details of the atomization approach are given in Appendix B.

TABLE I
APPROACHES TO TELLURIUM PARTICLE SIZE ANALYSIS

Technique	Principle	Problems	Comments
Coulter	Electrolyte resistivity changes in a small volume dependent on particle size	Large particles selectively settle from the electrolyte	Proved valuable on powders under ~40 μm
Zeiss	Optical comparison to photomicrographs	Must photographically resolve particles without agglomeration	Proved valuable on coarser powders
Micromerograph	Stoke's law sedimentation in air	Air exposure of Te posed toxicity problem	Not used
Sedigraph	Stoke's law sedimentation in liquid	Limited to size range 0.2 to 50 μm , must know some powder characteristics	Did not break apart agglomerates
Sedibal	Same	Requires extensive calculations to perform an analysis	Not used
Centrifuge	Same	Same	Same
Precision screening	Collect particles on stacked screens with known openings	Screens become blocked with fines; must be used in glove box	Did not separate fines from coarse

Figure 1. Scanning Electron Micrographs of Commercial Te Powders

- (a) Attritioned and screened Te powder illustrating the angular particle shape and adherent fines (100 X)
- (b) Electrochemical precipitated Te powder showing the very fine particle size (10,000 X)

Figure 2. Atomized Te Powder Before Air Classification (200 X)
 (Material source - Kawecki Berylco, Purity - 99.99% Te,
 S - 0.15 m²/g, and $\bar{d}_N$ - 6.3 μm)

Powder Classification

The four techniques listed in Table II were applied to the classification of the Te powders. As a comparison aid, the specific surface areas and $\bar{d}_N$ values are listed by technique in Table II. Development of the appropriate separation approach was performed on a powder similar to that shown in Figure 1a. Examination of the micrographs in Figures 3 through 6 and consideration of the surface areas show that either ultrasonic agitation combined with wet sedimentation or air elutriation resulted in deagglomeration and significant fines removal. Air elutriation (classification) techniques are well-developed for powder materials and do not introduce the potential contamination of the wet sedimentation technique. Hence air classification is the preferred approach. An important point is that screening is not an appropriate classification technique for irregular shaped Te powder.

Development of an Optimal Tellurium Powder

The justification for the powder characterization, fabrication, and classification development work was the eventual separation of an optimal Te powder for thermite reactions. Elimination of the fines portion of the size distribution was intended to reduce instabilities in the long-term storage of thermite mixtures. As illustrated earlier, the specific surface area is a primary factor in establishing the chemical stability of a powder mixture. With respect to shape, a spherical particle is optimal. Not only does a sphere minimize the surface area-to-volume ratio, it is also the optimal shape for air classification. In addition, a sphere is most easily coated by chemical vapor deposition; thus, a spherical particle shape is amenable to metallic coatings if they are required to ensure long-term stability. Hence, it was decided to use the atomized Te for preparation of several "optimal" powders.

The powder atomization was achieved as outlined in Appendix B from a 99.99% pure Te stock. Subsequently, the atomized powder was separated by a combination of screening and air classification into the six size fractions listed in Table III. Scanning electron micrographs of these six size fractions are shown in Figures 7 through 12. The +300, 100 to 300, and -20 μm size fractions exhibited undesirable characteristics. The fines cut (-20 μm) contained numerous micron-sized particles. The coarser particles (over 100 μm) were composed of many agglomerates and irregular shaped particles. The agglomerated fine particles account for the higher-than-expected surface area for the +300 μm size fraction. Because of these undesirable properties, there was no further characterization of these three fractions. For the remaining three fractions, particle size distributions were determined from scanning electron micrographs by means of the Zeiss particle size analyzer.

TABLE II
TELLURIUM POWDER CLASSIFICATION APPROACHES
Starting powder - irregular particles, source - ROC/RIC
screened 44 to 150 μm
 $S = 0.33 \text{ m}^2/\text{g}$
 $\bar{d}_N = 2.9 \mu\text{m}$

Technique	Details	Result	$S, \text{m}^2/\text{g}$	$\bar{d}_N, \mu\text{m}$	Figure No.
Screening	Agitated powder over screens to remove -44 + 37 μm	Agglomerates, adherent fines	0.41	2.3	3
Water wash	Stirred powder slurry, decanted fines, and repeated three times	Eliminated agglomerates, considerable adherent fines remained	0.33	2.9	4
Air elutriation	Classification by creating air flow which shears fines from powder surface (repeated 3 times)	Good, no agglomerates, few fines	0.15	6.4	5
Ultrasonic agitation plus wet sedimentation	Added Daxad 23 as wetting agent to wet powder, ultrasonic plus decant fines (repeat 3 times)	Few fines, no agglomeration	0.12	8.0	6

Figure 3. Te Powder Classified Into a -44 +37 μm Size Fraction by Screening; Fines Not Removed (1000 X)
(Material source - Research Inorganics (ROC/RIC), and purity - 99% Te)

Figure 4. Te Powder Classified by Repeated Water Washings; Fines Not Removed (1000 X)
(Material source - Research Inorganics, Purity - 99% Te, and Screened - -150 +44 μm)

Figure 5. Te Powder Classified by Repeated Air Elutriation; Fines Removed (300 X)
(Same starting material as shown in Figure 4)

Figure 6. Te Powder Classified by Ultrasonic Agitation of a Liquid Slurry Followed by Wet Sedimentation; Majority of Fines Removed (300 X)
(Same starting material as shown in Figures 4 and 5)

Figure 7. +300 μm Spherical Te Powder (500 X)

Figure 8. 100 to 300 μm Spherical Te Powder (100 X)

Figure 9. 53 to 100 μm Spherical Te Powder (100 X)

Figure 10. 37 to 53 μm Spherical Te Powder (100 X)

Figure 11. 20 to 37 μm Air Classified Spherical Te Powder (300 X)

Figure 12. -20 μm Air Classified Spherical Te Powder (1000 X)

The particle size distributions are shown in Figure 13, and the mean sizes are listed in Table III. For comparison, the Zeiss distribution for the air-elutriated irregular Te powder (see Figure 5) is also shown in Figure 13. Unfortunately, the Zeiss technique ignores any adherent fines, and thus the tabulated values are much larger than those listed as $\bar{d}_N$. Optical metallography revealed an internal porosity in the atomized powders, as illustrated in Figure 14. These voids represent shrinkage induced porosity associated with particle solidification. Polarized light microscopy quite successfully resolved the grain structure in these particles, as illustrated by Figure 15. The grain size was typically less than 10 μm for all three powder fractions.

The three intermediate size classifications (20 to 37, 37 to 53, and 53 to 100 μm) represent near optimal Te powders. These powders provide a systematic increase in particle size, suitable for experimental determination of the thermite reaction property variations with particle size. Future efforts should be aimed at determining the particular particle size that provides the proper compromise between thermite reaction kinetics and long-term stability. If deemed necessary by future studies, these powders can be chemically vapor deposited with a stable metallic coating to enhance stability. An example of tungsten coated Te (thermally cracked $\text{W}(\text{CO})_6$ deposited on the 53 to 100 μm Te) is shown in Figure 16a. One problem with this approach is the lack of coating adhesion, as illustrated in Figure 16b.

Summary

The characteristics of optimal Te powders for thermite-type reactions have been identified. The dominant concern is with the specific surface area. The technology involved in the production of "optimal" Te powders is described in detail. Fabrication of spherical Te powders has been achieved by argon atomization of liquid Te. The atomized material has been successfully classified into narrow size ranges by air classification with significant removal of adherent fines. The minimum powder characterization consists of examination by scanning electron microscopy coupled to nitrogen adsorption surface area determination. Future experiments should utilize the three "optimal" powder fractions described in this report to establish a particle size influence on the thermite reaction variables.

Figure 13. Ziess Particle Size Distributions for the Three Spherical Te Powders Shown in Figures 9, 10, and 11, and the Air-Elutriated Irregular Te Powder Shown in Figure 5.

TABLE III
CLASSIFIED ATOMIZED TELLURIUM

Material Source - Kawecki Berylco
Atomized - Special Metals
Purity - 99.99% Te
Classified - Battelle Columbus

Size Range	S, m ² /g	$\bar{d}_N$, μm	Mean Size Zeiss Analysis, μm	Figure Number	Comments
+300 μm	0.051	18.9	Not measured	7	Agglomerates and coarse particles
100 to 300 μm	0.035	27.2	Not measured	8	Many flakes
53 to 100 μm	0.048	19.9	80	9	Uniform size, mostly all spheres
37 to 53 μm	0.062	15.4	48	10	Uniform size, some agglomerates
20 to 37 μm	0.089	10.8	33	11	Uniform
-20 μm	0.237	4.1	Not measured	12	Spherical, wide size range, some very fine

Figure 14. Optical Micrograph of Polished Cross Sections Through the 53 to 100 μm Te Spheres (400 X)

Figure 15. Polarized Light Micrograph Showing the Grain Structure in the 53 to 100 μm Spherical Te Powder (800 X)

Figure 16. 53 to 100 μm Spherical Te Coated With Tungsten:
 (a) 300 X and (b) 1000 X

APPENDIX A

POWDER CHARACTERIZATION TECHNIQUES OUTLINE

Specific Surface Area

The specific surface area was measured using nitrogen absorption in accordance with the BET technique.⁸ The measurements were performed on a Quantachrome Quantasorb surface area analyzer. Prior to analysis, each sample was outgassed by heating at 200°C for 2 hours in flowing dry nitrogen. The surface area was determined by adsorbing nitrogen from a nitrogen plus helium gas mixture. Adsorption was measured by monitoring the gas mixture thermal conductivity. All adsorption measurements were performed at 77K, using N₂/He ratios of 2/18, 4/16, and 6/14 (i.e., three point BET). The instrument settings and calculation constants for these determinations were optimized as: attenuation = 8, bridge current = 180 ma, calibration volume = 0.06 cm³, saturation vapor pressure = 102 kPa, molecular weight of adsorbate = 28, and adsorbate cross sectional area = 16.2 x 10⁻²⁰ m². The specific surface area was calculated from the three-point adsorption measurements.⁹

Coulter Counter Particle Size Analysis

The Coulter Counter provides a particle size distribution on either a weight or population basis. The size measurement is performed by passing an electrolyte containing the dispersed powder through a small aperture. Resistivity changes induced by particle motion through the aperture can be directly related to the particle size.⁹ The analyses at Sandia were performed on a Model TA-II instrument with a 100 μm aperture tube (size range 2 to 40 μm). A 3 % NaCl electrolyte was used for all analyses. The powder samples were dispersed in electrolyte using 3 drops each of 1 wt. % Calgon and 1 wt. % Daxal 23 in 20 ml fluid. The sample was ultrasonically agitated for a total of 80 minutes prior to analysis. The instrument was calibrated with 3.49 μm latex spheres.

Zeiss Particle Size Analysis

The Zeiss particle size analysis uses a simple light system to optically sort photomicrograph images into appropriate size classes.

Scanning electron micrographs with known magnifications were manually analyzed using the Zeiss instrument to establish particle size distributions. Colloidal graphite was used to ensure specimen conductivity and adhesion to the substrate in the microscope.

APPENDIX B

TELLURIUM ATOMIZATION

Tellurium raw stock in the form of 1-cm pieces was purchased from Kawecki Berylco Industries, Penn Rare Metals Division, Revere, PA. The material was 99.99% pure Te, containing only Se as a significant impurity (~50 ppm). The atomization was performed by a proprietary gas atomization process at Special Metals, Udimet Powder Division, Ann Arbor, MI. Five-kg batches of the Te material were induction melted in a clay-graphite crucible. Charcoal was floated on top of the liquid Te to prevent oxidation. Atomization was performed at 600°C using pressurized argon and a zirconia/alumina nozzle. The molten Te was atomized into a 0.38 m³ barrel that contained approximately 5 x 10⁻² m³ of water to aid in powder recovery. The molten Te seemed to wet the nozzle assembly, which caused difficulty in maintaining a uniform atomization. Three different atomization conditions were studied as identified in Table A-I, and lot 2 was used for the subsequent studies.

TABLE B-I
ATOMIZATION RESULTS

Lot	Specific Surface Area
1	0.201
2	0.112
3	0.153

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