AUG 27 1968

AEC RESEARCH AND DEVELOPMENT REPORT

Y-1476

Chemistry

MASTER

PREPARING AND SINTERING TUNGSTEN POWDER

C. R. Schmitt
L. R. Phillips
J. M. Googin
C. F. Piper

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

Y-12 PLANT
Oak Ridge, Tennessee

**UNION
CARBIDE**

UNION CARBIDE CORPORATION
NUCLEAR DIVISION

Operating the

OAK RIDGE GASEOUS DIFFUSION PLANT • OAK RIDGE NATIONAL LABORATORY
OAK RIDGE Y-12 PLANT • PADUCAH GASEOUS DIFFUSION PLANT

*For the Atomic Energy Commission
Under U.S. Government Contract W7405 eng 26*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in USA. Price \$3.00. Available from the Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U.S. Department of Commerce, Springfield, Virginia

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Date Issued: August 20, 1965

Document Number Y-1476

Chemistry
TID-4500 (41st Edition)

UNION CARBIDE CORPORATION
Nuclear Division

Y-12 PLANT

Contract W-7405-eng-26
With the US Atomic Energy Commission

PREPARING AND SINTERING TUNGSTEN POWDER

C. R. Schmitt
L. R. Phillips
J. M. Googin
C. F. Piper

Oak Ridge, Tennessee
March 26, 1965

Document Number Y-1476Chemistry
TID-4500 (41st Edition)

Distribution:

Bailey, E. W.		Lang, D. M.	(ORGDP)
Ballenger, H. F.	(2)	Marrow, G. B.	
Briscoe, O. W.		McLaughlin, L. M.	
Burkhart, L. E.		McLendon, J. D.	
Center, C. E.	(ORGDP)	Mitchel, G. W.	
Christman, A. M.		Neeley, A. C.	
Cowen, D. D.	(ORNL)	Patton, F. S.	
Dow, Neal		Phillips, L. R.	
Fortenbery, M. J.		Piper, C. F.	
Googin, J. M.		Schmitt, C. R.	(10)
Harwell, W. L.	(ORGDP)(5)	Schreyer, J. M.	
Hemphill, L. F.		Waters, J. L.	
Huber, A. P.	(ORGDP)	Whitson, W. K.	
Humphreys, H. M.	(UCC-NY)	Winkel, R. A.	(Paducah)
Keller, C. A.	(AEC-ORO)(4)	Yaggi, W. J.	
Kite, H. T.		Zurcher, E.	
Lewis, F. O.	(ORGDP)	Y-12 Central Files	(5)
Lambdin, F.		Y-12 Central Files	(Y-12RC)

In addition, this report is distributed in accordance with the category Chemistry, as given in the "USAEC Standard Distribution Lists for Unclassified Scientific and Technical Reports", TID-4500 (41st Edition), May 1, 1965.

ABSTRACT

Variables affecting the production of a sinterable, high-purity, tungsten metal powder by the hydrogen reduction of tungsten oxides have been studied; and ultra-fine tungsten powder, sub-micron in size, with high surface areas ranging from 5 to 15 square meters per gram, have been prepared.

Sintering tests on isostatically pressed compacts made from these powders showed that a density that is 95 - 98% of the theoretical density can be obtained by sintering for three hours at 1500° C in a flowing hydrogen atmosphere. This level is much better than the approximately 80 - 85% of the theoretical density obtained from compacts made from a typical, fine, commercially available tungsten powder having a surface area of 0.2 square meter per gram sintered under equivalent conditions.

Studies show that when tungsten oxides are reduced with hydrogen under increasing reduction temperatures in the range between 700 - 850° C, a decrease occurs in the surface area of the resulting tungsten powders. Sintering tests on pressed compacts made with these powders also showed that a high reduction temperature has an adverse effect on the sintered density.

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

CONTENTS

INTRODUCTION	7
SUMMARY.	9
EXPERIMENTAL WORK	11
Equipment and Procedures	11
Preparing Tungstic Oxide	11
Introduction	11
Wet Chemical Precipitation	11
Ion-Exchange Precipitation	13
Preparing Tungsten Metal	13
Preparing Powder Compacts	15
Die Pressing	15
Isostatic Pressing	17
Sintering	19
Process Variables.	19
Equipment and Procedures	21
Investigation of Process Variables	23
Physical Properties of Commercial and Laboratory-Prepared Tungsten Powders.	23
Hygroscopicity of Tungstic Oxide	28
Reduction of Ammonium Paratungstate	28
Reduction of Tungstic Oxide	35
Effect of Temperature	35
Relationship of Surface Area to Crystallite Size.	35
Relationships of Surface Area to Free-Flow and Tap Densities	37
Effect of Water Vapor.	38
Effect of Oxide Particle Size	41
Properties of Freshly Reduced Powder	42
Pyrophoricity and Hygroscopicity	42
Oxygen Pickup During Compaction	44
Relationship of Oxygen Content and Surface Area.	44
Relationship of Nitrogen and Oxygen Content	44
Relationship of Surface Area and Green Compact Density	45
Removal of Carbon from Tungstic Oxide.	46
Removal of Carbon from Tungsten Powder	47
Sinterability	48
Effect of Time at the Sintering Temperature	48
Effect of the Reduction Temperature and Moisture Removal	48
Effect of the Forming Pressure	52

Effect of High-Pressure Compaction	53
Effect of Oxygen	54
Effect of Nitrogen	58
Effect of Additives	65
Effect of Oil Contamination	69
Shrinkage and Densification	70
Improving the Sinterability by Post-Reduction Treatment.	71
Chemical Purity	72
Improving the Sinterability of the Commercial Powders	74
Microstructure	76
Photomicrography	76
Fractography and Electron Microscopy.	81
 DISCUSSION	 85
 ACKNOWLEDGEMENTS.	 87
 REFERENCES	 89
 APPENDIX (ANALYTICAL PROCEDURES)	 91
Physical Methods	93
Particle Size Distribution	93
BET Surface Area	93
Density by Helium Displacement	94
Crystallite Size	94
Determination of the Sintered Density	95
Chemical Methods	95
Nitrogen	95
Carbon.	96
Oxygen	96

INTRODUCTION

Since tungsten has the highest melting temperature ($3410 \pm 20^\circ \text{C}$) of all the metals and has a high strength at elevated temperatures, it has assumed major importance as a structural material for high-temperature applications, particularly in the fields of space-age rocketry⁽¹⁻⁴⁾ and advanced nuclear reactors. Although in recent years techniques involving arc and electron-beam melting and casting have been used for the purification and consolidation of tungsten, the major method used commercially is by pressing tungsten powders and sintering them at high temperatures.⁽⁵⁻⁷⁾ This method also offers the advantage of some grain-size control.

In the fabrication of high-density tungsten bodies by powder-metallurgical techniques, the physical and chemical characteristics of the powder are of utmost importance. Even though these characteristics are established by the processing history of the metal from the ore to the powdered metal state, the final reduction step is the most important.

In the commercial production of pure tungsten metal, hydrogen is almost always used for reducing an intermediate tungsten compound; eg, tungstic oxide or ammonium paratungstate (APT), to the metal because almost any other reducing agent would leave impurities. Historically, tungsten powder for use as electric lamp filaments was first prepared commercially by reducing the oxide with carbon; however, the resulting powder was rather impure. The commercial preparation of tungsten powder by reducing tungstic oxide (WO_3) or tungstates with hydrogen (begun about 1912) yielded a purer metal powder and also permitted a closer control of the particle size.

A review of earlier literature concerning the equilibrium between tungsten metal and its oxides in an atmosphere of hydrogen and water vapor is given by Kopelman.⁽⁸⁾ Considerable controversy concerning the chemical composition of the oxide intermediate between WO_3 and WO_2 is indicated. The equation for the reduction reaction in its entirety may be written as:

Thus, if the water vapor is removed continuously from the reaction zone and hydrogen is supplied, the reaction should proceed toward the right.

According to Smithells⁽⁹⁾ and Li and Wang,⁽¹⁰⁾ the particle size of the tungsten powder is determined to a large extent by the particle size of the intermediate tungsten compound and upon the reduction conditions employed. Major reduction variables affecting particle sizes are: temperature and time of reduction, state of subdivision of the original oxide, and concentration of water vapor in the hydrogen.⁽⁹⁻¹²⁾ Smithells⁽⁹⁾ reports that, "by carefully controlling these variables the powder produced can be varied from a fine, black, pyrophoric material in which the mean

diameter of the particles is less than 0.5μ to coarse metal crystals up to 500 microns in diameter".

Considerable experience has been gained at the Y-12 Plant with cold pressing commercially available tungsten powder. Metal having a particle-size range of 1 to 5 microns and a surface area of approximately 0.2 square meter per gram requires sintering temperatures in excess of 2400°C to produce metal compacts having densities not in excess of 17.5 gm/cc , or approximately 90% of the theoretical density. These findings are in general agreement with the experience of the United States tungsten industry which has reported that sintering treatment in an atmosphere of pure hydrogen at temperatures in the range between $2700 - 3100^{\circ}\text{C}$ ($4900 - 5600^{\circ}\text{F}$) gave final sintered bars having a density between 90 and 95% of the theoretical value. (6)

In the process of sintering metal powder compacts, a migration of atoms occurs between neighboring particle surfaces. Therefore, the formation of sinter bonds between powder particles would be expected to be greatly facilitated by the use of relatively fine powders. Since the finer the powder the greater the amount of exposed surface, a more intimate contact would be provided for fine particles than for coarse particles, and more surface energy would be released. Thus, it is generally believed that if an ultra-fine tungsten powder having a high surface area (ie, $5 - 15 \text{ m}^2/\text{gm}$) is made available, the sintering temperature could be lowered to $1500 - 2000^{\circ}\text{C}$, thereby effecting substantial production economies and producing materials with more desirable properties and greater purity.

Accordingly, a laboratory program was initiated at Y-12 for investigating the variables involved in the production of tungsten metal powder having a suitably high surface area and chemical purity; one which could be used for the preparation of high-density, sintered metal compacts. Small pellets ($\sim 1/2" \times 1/2"$) were pressed from tungsten powder prepared in the laboratory, then sintered in a flowing hydrogen atmosphere for 3.0 hours at 1500°C .

SUMMARY

Variables affecting the production of a sinterable, high-purity tungsten metal powder by the reduction of tungsten oxides with hydrogen have been studied. In general, ultra-fine tungsten powders, submicron in size and having relatively high surface areas (ranging from 5 to 15 m²/gm) have been prepared.

Sintering tests on small compacts pressed isostatically from the ultra-fine powders have shown that metal derived from tungstic oxide prepared by wet chemical methods of precipitation sinters to approximately 95 - 98% of the theoretical density in three hours at 1500° C in a flowing hydrogen atmosphere. Only about 85% of theoretical density is obtained in compacts made from typical, fine, commercially available tungsten powder having a surface area of 0.2 square meter per gram. Compacts made from powder prepared by the reduction of commercial ammonium paratungstate or of tungstic oxide derived from commercial ammonium paratungstate gave sintered densities approximately 90% of the theoretical value under equivalent surface area and sintering conditions.

A study of the effect of the reduction temperature on particle size showed that a decrease in the surface area occurred when the reduction temperature was increased in the range between 700 - 850° C.. Sintering tests on pressed compacts made with these powders similarly showed an adverse effect on the sintered density by a high reduction temperature.

The presence of water vapor in the hydrogen also had a pronounced effect on the resulting metal powder during reduction. Since water vapor is a product of the reduction reaction, which is reversible at elevated temperatures, it was necessary to employ a very rapid flow of hydrogen gas to keep the water vapor concentration minimal.

The oxygen content of tungsten powder was also found to be related to the surface area of the powder. Oxygen pickup occurred extensively upon exposure of the freshly reduced high-surface-area powder to the atmosphere. In many instances the exothermic surface oxidation reaction produced pyrophoricity despite the prior removal of occluded hydrogen from the powder by extensive purging and vacuum treatment.

The surface area and sinterability of commercial tungsten powder was upgraded considerably by oxidizing it to tungstic oxide at 500° C and reducing it with hydrogen at 700° C.

A high oxygen content of the tungsten powder, presumably present as an oxide coating, was found to have a serious adverse effect on the sintered density. A study of the effect of nitrogen on sintered density showed that it is readily liberated from tungsten at elevated temperatures and is not detrimental in small amounts; ie, 50 ppm. In studying this effect, several attempts were made to prepare tungsten nitride by

the reaction of nitrogen gas, arced nitrogen, and ammonia at various temperatures from 25 to 1500° C. The highest nitride content obtained was only 0.18%.

Effective removal of carbon from a batch of carbon-spiked tungstic oxide was accomplished by air oxidation at 500° C and from carbon-spiked tungsten powder by treatment with hydrogen at 1100 - 1500° C.

EXPERIMENTAL WORK

EQUIPMENT AND PROCEDURES

Preparing Tungstic Oxide

Introduction - Preparing tungstic oxide powders by controlled precipitation methods designed to produce both high surface area and high chemical purity has been studied at Y-12. Oxide surface areas ranged from 5 to 50 square meters per gram. A schematic representation of the wet-chemical precipitation and ion-exchange methods for preparing high-surface-area, high-purity WO_3 from commercial ammonium paratungstate is shown in Figure 1. As indicated, this method involves a series of precipitation and dissolution steps from acidic and basic media, provides good purification, and permits a control of particle size and agglomerate structure during the final precipitation step.

Wet Chemical Precipitation - In this method, ammonium paratungstate (APT) crystals are added to a four-molar nitric acid solution with rapid agitation at approximately 60°C . This produces a slurry of tungstic acid (hydrated WO_3) which is filtered, and the filtrate discarded. After rinsing the solids with water, the tungstic acid is slurried in distilled water and heated to 60°C . Ammonium hydroxide is added until a $\text{NH}_3:\text{WO}_3$ molar ratio of 4:1 is attained. This dissolves the tungstic oxide and produces a solution of ammonium tungstate containing 100 to 300 grams of tungstic oxide per liter. The ammonium tungstate solution is filtered to remove insoluble impurities and any unconverted APT.

The final precipitation is made by adding ammonium tungstate solution at a constant rate of 15 - 25 milliliters per minute to the side of the vortex in rapidly agitated concentrated nitric acid ($> 4 \text{ M HNO}_3$) in a four-liter Pyrex beaker. The ammonium tungstate solution contained in a cylindrical separatory funnel is positioned to feed directly into the vortex of the concentrated nitric acid solution by using a short length of Tygon tubing and a medicine-dropper tip. Agitation is provided by a 1/4-inch-diameter stainless steel shaft fitted with three 1/2-inch round propeller vanes spaced equidistantly near the bottom of the shaft. The shaft is powered by a variac-controlled constant-torque electric motor, and a speed of 560 rpm is used during precipitation.

This arrangement provides essentially rapid mixing and precipitation under constant and reproducible conditions. As soon as the nuclei of tungstic acid forms, they are immediately removed from the reaction zone, thereby preventing large crystal growth. Accordingly, a very finely divided precipitate of hydrated tungstic oxide is obtained. This material is promptly filtered and washed, then dried to the tungstic oxide.

Figure 1. PREPARATION OF HIGH-SURFACE-AREA TUNGSTIC OXIDE.

Ion-Exchange Precipitation - In this method, a sodium tungstate feed solution, approximately 0.2 or 0.3 molar, is passed through a bed of Dowex 50W-X8 cation-exchange resin in the hydrogen form. Using a column residence time of approximately 0.5 hour, a colloidal tungstic acid ($\text{WO}_3 \cdot x\text{H}_2\text{O}$) is produced that has a particle size in the millimicron range. On standing, the liquid effluent from the column changes to a solid gel. The time for gelation is a function of both the tungstic oxide concentration and the temperature. A feed concentration as high as 0.35 M sodium tungstate will not plug the resin bed even at a flow rate of two column volumes per hour.

The tungstic acid slurry obtained by either the wet-chemical or ion-exchange precipitation methods is then filtered under vacuum using a Büchner funnel and Whatman 50 filter paper. The wet cake is washed with distilled water to remove any residual ammonium nitrate, dried in an oven to the oxide by heating to 130 - 140° C for eight hours, and calcined at 300° C for eight hours to decompose any traces of residual ammonium nitrate.

Preparing Tungsten Metal

Variables affecting the preparation of a high-surface-area tungsten powder (5 - 15 m^2/gm) by the hydrogen reduction of commercially available APT, and of various preparations of tungstic oxide, have been investigated using the apparatus shown in Figure 2.

A charge of APT or tungsten oxide (usually approximately 50 grams) was placed into a shallow quartz boat (1" W x 3/8" H x 20" L) and set inside of a 1.5-inch-diameter by a 60-inch-long quartz reduction tube. The tube was heated electrically by a clam-shell furnace, and temperature control was provided by a Leeds and Northrup Model H controller. A flow of purified hydrogen gas was passed over the charge at a specified temperature (700 - 850° C) for various intervals of time. Commercial hydrogen gas supplied in 2000-psi cylinders was purified by passing it through a Deoxo unit and a Drierite bed, then over a bed of titanium sponge maintained at 850 - 900° C.

The Deoxo unit contains a platinum catalyst which causes any oxygen impurity to react with the hydrogen to form water vapor. The calcium sulfate (Drierite) removes the water vapor. A Molecular Sieve trap is used as a backup trap for any residual water vapor not removed by the Drierite trap. In the final purification stage, the hot titanium sponge acts as a "getter" for any remaining traces of water vapor, oxygen, and nitrogen.

The exhaust gases from the reduction furnace were ignited to provide a safe method for the disposal of the excess hydrogen. A glass medicine-dropper tip was attached to the outlet gas line with gum rubber tubing. After purging the apparatus with helium, hydrogen was admitted to the reactor. The outlet gas stream was periodically checked with a flame until the gas ignited. Further checking was not required as

Figure 2. APPARATUS FOR PREPARING TUNGSTEN POWDER.

long as the hydrogen gas flow was maintained. By coating the medicine-dropper tip with a few drops of sodium chloride, the hydrogen flame burned with a yellow coloration and thus was made visible.

At the completion of the reduction reaction, the quartz tube was cooled to 50 - 100° C, while a flow of hydrogen was maintained. The tube was then purged with helium and evacuated to $< 10 \mu \text{ Hg}$ for sixteen hours in an attempt to remove any occluded hydrogen. The application of vacuum to the freshly reduced tungsten powder prior to exposure to air was found to be necessary in order to reduce the pyrophoricity of the fine metal powders. The tube was unloaded after being brought slowly to atmospheric pressure by bleeding in air.

A schematic diagram that summarizes the various processing steps used in the reduction of tungstic oxide by hydrogen along with the tungsten powder metallurgy operation, is shown in Figure 3.

Preparing Powder Compacts

Die Pressing - Tungsten powder compacts (pellets) have been molded by two methods, die pressing and isostatic pressing. In the first method, tungsten powder is loaded into a cylindrical, hardened-steel die of 0.5-inch diameter. A photograph of the die-pressing mold, showing assembled and exploded views, is given in Figure 4. Pressure is applied at 30,000 psi using a hydraulic press. (a) The bottom ram is positioned in the die by covering the base of the die with a sponge rubber insert (not shown in Figure 4) approximately 1/4-inch thick and having a 1/2-inch-diameter center hole. Experience shows that the extremely fine particle size and abrasive nature of some of the laboratory-prepared batches of powder causes difficulties with scoring, galling, and seizure of the top ram when these powders are pressed at 30,000 psi.

Although die seizure is decreased somewhat by the use of stearic acid as a lubricant, the probability of contamination of the tungsten pellet by the lubricant is also introduced. Prepressing the tungsten powder at a lower pressure (ie, approximately 5000 psi), followed by grinding with a mortar and pestle, and screening through a 40 mesh screen, is also effective in eliminating die seizure, but has the disadvantage of contamination due to increased powder handling.

Compressing a powder contained in a cylindrical die cavity by applying the forming pressure in a single direction also results in compression layers or laminations, and a distribution in density occurs between the center and ends of the compact. This disadvantage, in addition to die seizure, is eliminated by isostatic pressing the tungsten powder.

(a) Model B, manufactured by Fred S. Carver, Inc.

106162(U)

Figure 4. PELLET DIE-PRESSING ASSEMBLY.

Isostatic Pressing - Isostatic pressing is a method for compacting powdered materials by applying the hydraulic force of a liquid (such as water or mineral oil) on the powder enclosed on a thin-walled elastomeric bag. The bag (usually rubber or plastic) separates the powder from the liquid and also serves as a rough mold. Pressure is exerted equally over the entire surface of the mold, providing uniform compaction of the powder from top to bottom as well as from all sides. Strains, cracks, or laminations usually associated with die pressing can be largely eliminated from the pressed compacts by this method of pressing.

Using the isostatic method, the tungsten powder is pressed into small compacts (pellets) at 30,000 psi using the procedure outlined in the sections that follow.

Mold-Loading Operation - Figure 5(a) shows the mold-loading operation. A piece of filter paper is placed in the bottom of a stainless steel shaping mold which is seated on the vacuum tubing. Vacuum is then applied through the pinhole in the bottom of the shaping mold to hold the mold in place. A latex surgical finger cot or a thin Visten^(b) film bag, having a wall thickness of approximately five mils, is partially unrolled, inserted into the shaping mold,

(b) Visten, a seamless, thin-wall plastic manufactured by the Visking Company, a Division of Union Carbide Corporation.

Figure 5. MOLD LOADING, MOLD SEALING, AND ISOSTATIC PRESSING OPERATIONS.

and the band at the open end stretched over the top of the shaping mold. The vacuum then causes the finger cot to stretch and fit snugly to the walls of the shaping mold.

With the vacuum on, tungsten powder is added slowly by means of a spatula. The powder is packed down between each addition by gentle vibration that is

applied by tapping the sides of the stainless steel shaping mold and by tamping the powder down with a tapered rubber stopper. After filling the finger cot with powder, a rubber disc approximately 1/8-inch thick, cut from the top of a rubber stopper, is then placed on top of the powder and pressed down firmly. The band of the latex finger cot is then rolled out to its full length.

Mold-Sealing Operation - The mold-sealing operation is shown in Figure 5(b). A second piece of vacuum tubing is brought to the open end of the latex finger cot and the band of the cot is pulled over the end of this tubing. After the unrolled portion of the latex cot is collapsed by the vacuum it is sealed off by rotating the vacuum tubing which twists the end of the cot. The encapsulated tungsten powder and rubber disc are then vacuum sealed by tying a loop knot in the twisted end of the cot just above the filled portion.

Pressing Operation - After the tungsten powder pellet is sealed in the latex finger cot, it is dropped gently into a pressure vessel filled with light mineral oil, as shown in Figure 5(c). By means of a hydraulic press, a pressure of 30,000 psi is applied and maintained for approximately 30 seconds. A photograph of the isostatic vessel positioned on the hydraulic press is shown in Figure 6. A cutaway view of the isostatic pressure vessel is presented in Figure 7.

The pressed pellet is removed from the latex finger cot by cutting off the knotted end and peeling back the latex that adheres to the sides of the pellet. The pellet is then scribed with an identification number before sintering.

In a related study of isostatic-pressing techniques on tungsten and other refractory metal powders by Asbury,⁽¹³⁾ many large and small specialized items of equipment having various complex geometries have been fabricated by isostatic pressing and sintering.

Sintering

Process Variables - In sintering, a number of characteristic phenomena occur, principally shrinkage of the compact and changes in the microstructure caused by recrystallization and grain growth.⁽¹⁴⁾ Shrinkage is also affected by the density of the initial powder compact (ie, whether it is loosely or heavily compacted) and the purity of the powder.

The variables of time and temperature act in the same direction during sintering. The longer the time of heating, the better the mechanical coherence of the compact for a given temperature; the higher the temperature, the better coherence for a given period of heating. However, the effect of long times generally becomes less marked at higher temperatures.

105442(U)

Figure 6. HYDRAULIC PRESS WITH THE ISOSTATIC PRESSURE VESSEL IN PLACE.

Figure 7. ISOSTATIC PRESSURE VESSEL.

In this study, pressure-compacted tungsten powders were sintered at 1500°C in a flowing hydrogen atmosphere. Because of the relatively small size of these compacts, only primary information on densification was obtained. An evaluation of mechanical properties was not made. A sintering hold time of 3.0 hours at 1500°C was chosen as an arbitrary standard for evaluating the sintered compacts.

Equipment and Procedures - Tungsten powder compacts ($\sim 1/2"$ by $1/2"$) were placed in Alundum boats and loaded into a four-tube electric furnace.^(c) This furnace, shown in Figure 8, used Morganite recrystallized alumina tubes and employed flowing, purified hydrogen gas for the sintering atmosphere. The hydrogen gas purification train, arranged in series, consisted of a Deoxo unit, a Drierite trap containing eight-mesh granules of indicating-grade calcium sulfate, a Linde Molecular Sieve trap, and a bed of titanium sponge maintained at $850 - 900^{\circ}\text{C}$.

After purification, the inert hydrogen entered a common manifold equipped with four mercury-seal stopcocks. The exhaust gases from the four tubes of the sintering furnace were bubbled through Pyrex traps containing light mineral oil. This arrangement provided a positive gas pressure throughout the system and facilitated equal gas

(c) Manufactured by the Burrell Company.

105439(U)

Figure 8. GLOBAR SINTERING FURNACE AND ASSOCIATED GAS-PURIFICATION EQUIPMENT.

flow rates through the four sintering tubes by adjusting the rate of bubbling through the oil.

The tungsten compacts were sintered for 3.0 hours at 1500° C. Approximately four to five hours were required for the heat-up cycle to attain this temperature. Typical temperature-time profiles for heating and cooling cycles obtained for the sintering furnace are plotted in Figure 9. Flowing purified hydrogen gas was used throughout the cooling cycle until the furnace had cooled to room temperature. The furnace temperature was measured potentiometrically using a PT/PT-10% Rh thermocouple.

Figure 9. SINTERING FURNACE PROFILES OF HEATING AND COOLING CYCLES.

INVESTIGATION OF PROCESS VARIABLES

Experimental results have shown that finely divided tungsten metal powder having high surface areas ($5 - 15 \text{ m}^2/\text{gm}$) may be produced from a variety of intermediate tungsten compounds by hydrogen reduction. Intermediate tungsten compounds studied were: (1) ammonium paratungstate (APT), (2) tungstic oxide (WO_3) derived from APT, (3) tungstic oxide produced by wet chemical methods in the laboratory and pilot plant by rapid precipitation from ammonium tungstate solution or by ion exchange, and (4) tungstic oxide produced by oxidation of commercial tungsten powder.

Physical Properties of Commercial and Laboratory-Prepared Tungsten Powders

Electron photomicrographs comparing typical batches of laboratory-prepared, high-surface-area tungsten powder and commercial tungsten powder at 6400 magnification are shown in Figure 10. These show that the particles of the laboratory prepared

powders are ultra-fine, submicron in size, and highly agglomerated. The commercial tungsten powders appear to be composed of much larger, individual particles.

Particle-size distribution analyses of the three typical commercially available fine tungsten powders, shown in Figure 11, indicate a median particle-size range of about 2 to 7 microns. These analyses were obtained with a Micromerograph^(d) in which frequency-sized determinations of the particles are made using air-sedimentation rates in accordance with Stokes law (see Appendix). Comparative distribution analyses of powders prepared during this investigation are not available since these powders are submicron in size (having a median particle size of approximately 0.1μ) which is below the range of the Micromerograph.

A summary of the physical properties of typical commercial tungsten powders is given in Table 1. In general, the commercial tungsten metal powders, with low surface areas ($0.1 - 0.7 \text{ m}^2/\text{gm}$), may be characterized by their gray appearance, whereas the high-surface-area tungsten powders ($> 1 \text{ m}^2/\text{gm}$) are coal black.

One commercial batch of tungsten powder (Company E) was found to be somewhat unusual in that it exhibited unusually high green strength and ease of compaction. A photomicrograph of this powder, Figure 12, shows the presence of numerous finger-like appendages or protuberances (as shown by arrows). Difficulty was encountered in getting all of the protuberances in focus as many more are present in the powder than is indicated by the photomicrograph.

The interlocking of these protuberances upon compaction probably accounts for the high green strength. Compressive strength studies by Montgomery⁽¹⁵⁾ on isostatically pressed compacts made with this powder showed it to have average strengths three times greater than other typical commercial tungsten powders. The surface area of this powder was $0.15 \text{ m}^2/\text{gm}$.

An interesting characteristic of the laboratory-prepared tungsten powders (surface area $> 1 \text{ m}^2/\text{gm}$) as contrasted to typical commercial tungsten powders (surface area $< 1 \text{ m}^2/\text{gm}$) is their tendency to form spherical agglomerates upon being rolled or tumbled. Some typical commercial and laboratory-prepared tungsten powders before and after tumbling are shown in Figure 13. As indicated in this figure, laboratory-prepared tungsten powders having surface areas ranging from 1.7 to $5.9 \text{ m}^2/\text{gm}$ and oxide contents ranging from 0.2 to 2.0% exhibit this property.

Large, well-defined agglomerates approximately $3/8$ inch in diameter have been formed in pilot-plant preparations of high-surface-area tungsten powders using a rotary reduction furnace.⁽¹⁶⁾ These large aggregates readily retained their spherical shape during mild sintering treatment in flowing hydrogen, and temperatures of $900 -$

(d) Manufactured by Sharples Corporation, Bridgeport, Pennsylvania.

(a) Company A

6019

(b) Company B, Type I

6020

(c) Company B, Type II

6021

(a) W-34

5729

(b) W-18

5722

(c) A-32

6025

(d) P-52A

6027

Figure 10. COMPARISON OF TYPICAL LABORATORY-PREPARED AND COMMERCIAL TUNGSTEN POWDERS. (6400X)

Figure 11. PARTICLE-SIZE DISTRIBUTION OF COMMERCIAL TUNGSTEN POWDERS.

15489

Figure 12. STRUCTURE OF COMMERCIAL TUNGSTEN POWDER (COMPANY E) HAVING HIGH GREEN-STRENGTH CHARACTERISTICS. (Bright Field Illumination; 1000X)

Table 1
PROPERTIES OF FINE COMMERCIAL TUNGSTEN POWDERS

Powder	Company A	Company B		Company C
		Type I	Type II	
Surface Area (m ² /gm)	0.266	0.136	0.726	14.9
Surface Area (m ² /cc)	52	27	141	288
Median Particle Size by the Micromerograph (microns)(1)	2.7	7.2	2.1	< 1
Oxygen (%)	0.062	0.072	0.221	1.3
Nitrogen (ppm)(2)	41	43	161	951
Carbon (ppm)	28	80	31	316
Average Crystallite Size (Å)				
High	1740	2400	1020	235
Low	1645	2350	1015	233
Average	1693	2375	1018	234
Helium Density (gms/cc)	19.31	19.27	19.26	16.8
Spectrographic Analysis (ppm)				
Ag	6	< 10	< 20	< 1
Al	< 30	< 40	< 40	25
Ca	30	< 100	< 100	10
Cu	6	< 10	< 10	< 1
Fe	150	100	< 100	60
Mg	30	< 100	< 100	< 1
Mn	< 10	40	< 40	< 3
Mo	< 30	400	250	200
Ni	< 30	80	60	30
Si	30	< 100	< 100	10
V	< 30	< 40	< 40	< 30
Zr	< 30	< 40	< 40	< 30

(1) Fifty percent of particles larger and 50 percent smaller. Data taken from particle-size distribution curves.

(2) By Kjeldahl method.

1500° C are enough to provide sufficient strength and stability to the spheres. Some typical macrosize spherical tungsten agglomerates, before and after sintering treatments, are shown in Figure 14.

It is believed that these spherical agglomerates are primarily bonded mechanically by an interlocking of the many individual powder particles into bridge-like agglomerates or "sponges". A photomicrograph of the bridge-like structure of the outer periphery of a tungsten ball formed by tumbling loose powder is shown in Figure 15.

A small batch of tungsten powder balls produced by tumbling 1 m²/gm tungsten powder was sintered for 3.0 hours at 1500° C in flowing hydrogen. These balls were then tumbled with some loose tungsten powder having a surface area of 6 m²/gm, and the resulting tungsten-coated, sintered tungsten balls were sintered for 0.5 hour at 1500° C in flowing hydrogen. This tumbling and sintering procedure was repeated until three coatings of tungsten powder had been deposited on the tungsten core

balls. A cross section of one of the balls, showing the lamellate structure, is shown in Figure 16.

A distinct differentiation of the three separate outer layers of tungsten could not be made. Cross-sectional metallographic studies, however, showed that the core tungsten has a much coarser grain size than the outer tungsten layers. This difference may have resulted from the fact that the lower surface area of the tungsten powder used for the core ball showed lower sinterability. Photomicrographs of cross sections of the inner case and outer periphery of the laminated tungsten balls showing the grain structure at 500 and 1000X are given in Figures 17 and 18.

By alternately tumbling and sintering fine tungsten powder with a core ball of sintered tungsten, the ball can be increased in size. It has also been demonstrated that the fine tungsten powder will readily adhere to core balls of many other materials that have a fairly rough surface; eg, naphthalene, aluminum oxide, and porcelain.

It was also found that the fine tungsten powder is very amenable to compaction by rolling with small sintered tungsten balls or cylinders. Upon coating some sintered tungsten balls in a six-ounce wide-mouthed glass jar in this manner, it was observed that a ring of compacted powder had formed at the neck end of the jar, as shown in Figure 19. This property of being easily tamped or compacted by rolling or tumbling may serve as the basis of a useful fabrication technique for making miscellaneous shapes and complex geometries.

Hygroscopicity of Tungstic Oxide

A 7.2-gram batch of relatively high-surface-area tungstic oxide ($30.3 \text{ m}^2/\text{gm}$) was spread out on a Petri dish having an area of three square inches and exposed to the atmosphere. After weighing at various intervals of time it was found that the tungstic oxide showed an overall weight gain of 0.3% after a three-hour static exposure period. Results, as summarized in Table 2, indicate that appreciable adsorption of moisture from the atmosphere was still occurring after a 30-minute exposure.

Similar exposure of a 4.5-gram batch of relatively low-surface-area tungstic oxide ($3.5 \text{ m}^2/\text{gm}$) showed a total weight gain of only 0.19% H_2O . Results, as given in Table 2, indicate that moisture adsorption was essentially complete after approximately 20 minutes. The tungstic oxide used for this test had been prepared by oxidizing a thin bed of commercial tungsten powder spread out in a silica dish in a muffle furnace for 30 hours at 500°C . The tungsten powder was stirred occasionally with a spatula to insure complete oxidation of the powder at the bottom of the dish.

Reduction of Ammonium Paratungstate

Ammonium paratungstate (APT) can be decomposed and converted to tungsten trioxide by heating in air at temperatures above 250°C , liberating water vapor and

14767

(a) Commercial Powder after Tumbling for Sixteen Hours (SA - $0.1 \text{ m}^2/\text{gm}$; O_2 Content - 0.02%)

14738

(b) Laboratory-Prepared Powder after Tumbling for Sixteen Hours (SA - $5.9 \text{ m}^2/\text{gm}$; O_2 Content - 2.0%)

14763

(c) Laboratory-Prepared Powder before Tumbling (SA - $1.7 \text{ m}^2/\text{gm}$; O_2 Content - 0.2%)

14737

(d) Laboratory-Prepared Powder after Tumbling for Sixteen Hours (SA - $1.7 \text{ m}^2/\text{gm}$; O_2 Content - 0.2%)

Figure 13. SPHERICAL AGGLOMERATIONS OF COMMERCIAL AND LABORATORY-PREPARED TUNGSTEN POWDERS. (10X)

106281(U)

Figure 14. MACRO-SIZED SPHERICAL TUNGSTEN POWDER AGGLOMERATES PRODUCED BY TUMBLING.

14790

Figure 15. CROSS SECTION OF THE OUTER PERIPHERY OF AN AGGLOMERATED TUNGSTEN POWDER BALL. (Bright Field Illumination; 1000X)

14911(a)

Figure 16. CROSS SECTION OF A SINTERED TUNGSTEN-COATED TUNGSTEN POWDER BALL SHOWING ITS LAMELLATE STRUCTURE. (Etch Polished; 35X)

Table 2
HYGROSCOPICITY OF TUNGSTIC OXIDE

Exposure Time (min)	Weight Gain			
	Type I(1)		Type II(2)	
	(mgs)	(%)	(mgs)	(%)
1	1.5	0.021	-	-
2	2.5	0.035	-	-
3	3.4	0.047	1.0	0.029
4	4.0	0.056	-	-
5	4.6	0.064	-	-
20	-	-	6.5	0.186
36	16.1	0.224	-	-
50	18.7	0.260	-	-
60	-	-	6.5	0.186
66	19.7	0.273	-	-
75	-	-	6.5	0.186
191	21.7	0.302	-	-

(1) Tungstic oxide surface area = $30.3 \text{ m}^2/\text{gm}$; amount of powder exposed = 7.2 gms.

(2) Tungstic oxide surface area = $3.5 \text{ m}^2/\text{gm}$; amount of powder exposed = 4.5 gms.

(a) 500X

14911(b)

(b) 1000X

14911(c)

Figure 17. CROSS SECTION OF THE INNER CORE OF A SINTERED TUNGSTEN POWDER BALL. (Etch Polished)

(a) 500X

14911(d)

(b) 1000X

14911(e)

Figure 18. CROSS SECTION OF THE OUTER PERIPHERY OF A SINTERED TUNGSTEN POWDER BALL. (Etch Polished)

14911(f)

Figure 19. LABORATORY-PREPARED TUNGSTEN POWDER ROLL THAT WAS TAMPED TO THE NECK OF A GLASS JAR. (3X)

ammonia as decomposition products. The tungstic oxide formed can then be reduced to tungsten metal with hydrogen, or the APT can be simultaneously decomposed and reduced to tungsten metal in a hydrogen atmosphere.

Table 3 summarizes the reduction data that were obtained for a run in which an APT-derived tungstic oxide and the final tungsten metal were compared with respect to surface area. When surface area is expressed in terms of square meters per gram, it would appear that a large increase in the surface area of the powder had occurred.

Table 3
SURFACE-AREA CHANGES ACCOMPANYING DECOMPOSITION
AND REDUCTION OF AMMONIUM PARATUNGSTATE

	BET Surface Area (m ² /gm)	Theoretical Density (gm/cc)	BET Surface Area (m ² /cc)
Original Ammonium Paratungstate (-325 mesh)	0.15	(1)	-
APT-Derived WO ₃ (air at 400° C)	7.06	7.16	50.5
Tungsten Powder (H ₂ at 800° C)	2.45	19.3	47.3

(1) Indefinite composition.

However, considering the large changes in particle density which also occur during the chemical conversion of APT to the oxide then to the metal, the apparent changes in surface area on a square-meter-per-gram basis are quite misleading.

Theoretically, a single particle of tungsten trioxide should decrease in volume upon reduction to tungsten metal. Since the density of the oxide is 7.2 gm/cc and of the metal is 19.3 gm/cc, it may be calculated that a single particle of tungsten oxide that is ten microns in diameter should produce a particle of tungsten metal 6.5 microns in diameter, if no interfering factors are present. Thus, surface-area changes between the oxide and the metal should be considered in terms of the more meaningful unit—square meters per cubic centimeter of theoretically dense material.

The surface area changes accompanying tungsten trioxide reduction are quite complicated, however, because many interfering factors must be considered; namely, agglomeration, porosity generation, oxygen content, grain coarsening by the volatility of the oxides, additives, and other sintering variables. Some of these variables in regard to tungsten have been discussed by Millner.⁽¹⁷⁾

Two methods of decomposing and reducing APT to tungsten metal powder with hydrogen were investigated briefly. In one method, decomposition and reduction were conducted at 400° C for several hours to produce a partially reduced oxide, possibly WO_{2.9} or WO_{2.75}, followed by hydrogen treatment at 750° C. In another method, the APT was decomposed and reduced in flowing hydrogen by heating to 750° C as rapidly as possible. Typical results, reported in Table 4, indicate that no significant differences in the surface area or sinterability of the tungsten powder product resulted from either treatment.

Reduction of Tungstic Oxide

Effect of Temperature - The effect of the reduction temperature on the surface area of tungsten powder was studied using a batch of tungstic oxide prepared by oxidizing commercial APT in a muffle furnace at 400° C. Reduction of this oxide at 700, 750, 800, and 850° C, under otherwise equivalent conditions, gave surface areas which decreased with increasing reduction temperature—from 10 to 2 m²/gm. Results are shown in Figure 20. A high reduction temperature was also found to have a serious adverse effect on sinterability, as will be discussed later.

Relationship of Surface Area to Crystallite Size - Crystallite sizes of the various batches of tungsten powders were determined from X-ray diffraction patterns by a line-broadening technique (see Appendix), and appear to provide useful information for predicting the general quality of tungsten powder with regard to sinterability. In general, the average crystallite size is inversely proportional to the BET surface area, as shown in Figure 21. These data represent batches of tungsten powder made at a reduction temperature of 700° C.

Table 4
COMPARISON OF SINGLE AND TWO-STAGE REDUCTION OF AMMONIUM PARATUNGSTATE

Type of Reduction	Reduction Conditions					Tungsten Powder			Sintered Density(1)	
	Charge (gms)	Screen Size (mesh)	Time (hrs)	Temperature (° C)	H ₂ Flow (liters/min)	(m ² /gm)	(m ² /cc)	(% O ₂)	(gms/cc)	(% TD)
Single Stage(2)	50	-150 + 200	5	750	4.4	7.56	146	0.75	17.0	89.3
Single Stage(2)	50	-150 + 200	8	750	4.4	5.6 - 7.4(3)	108 - 143(3)	1.1 - 1.3(3)	17.2	89.1
Two Stage(4)	50	-150 + 200	3 4	400 750	4.4	7.32	142	0.74	17.3	89.8
Single Stage(2)	50	-325	5	750	4.4	7.35 - 8.46(3)	142 - 163(3)	0.81 - 0.95(3)	17.3	89.8
Two Stage(4)	50	-325	3 6	400 750	4.4	6.23	120	0.90	17.5	90.8

(1) Sintered for 3.0 hours at 1500° C in flowing hydrogen.

(2) Simultaneous decomposition and reduction of APT.

(3) Powder sampled at gas outlet and inlet positions of boat, respectively.

(4) Decomposition of APT at 400° C prior to reduction.

Figure 20. EFFECT OF THE REDUCTION TEMPERATURE ON THE SURFACE AREA OF TUNGSTEN POWDER. (Starting Material was APT-Derived WO_3)

Relationships of Surface Area to Free-Flow and Tap Densities - The relationship between the surface area and the free-flow density and tap density of various batches of tungsten powder is indicated in Table 5. Although these data exhibit a considerable degree of scatter, it is indicated generally that those tungsten powders having a high surface area show a low free-flow and tap density, and those powders having a low surface area exhibit a high free-flow and tap density. As shown in Table 5, three typical commercial tungsten powders that were evaluated had surface areas less than $0.7 \text{ m}^2/\text{gm}$ and showed relatively high free-flow and tap densities. Since these rather coarse powders were shown to consist of relatively large, discrete particles, it is suspected that the low free-flow and tap densities shown by the powders having a relatively high surface area may be attributed to the highly agglomerated state of these powders.

The free-flow density was measured with a 10-milliliter graduated cylinder having a fluted opening. A known weight (~ 5 to 10 gms) of tungsten powder was poured into the cylinder through an 11-millimeter ID Pyrex funnel having a 60-degree slope. The powder was then leveled off with a spatula and the volume read directly from the cylinder to the nearest 0.1 cubic centimeter.

After completing the free-flow density measurement, the graduated cylinder was tapped gently on a hard table top until there was no apparent change in the powder volume. The tapped density was calculated as weight per unit volume.

Figure 21. RELATIONSHIP OF SURFACE AREA AND AVERAGE CRYSTALLITE SIZE OF TUNGSTEN POWDERS REDUCED AT 700°C.

Effect of Water Vapor - An attempt was made to increase the quantity of tungsten powder prepared with the hydrogen reduction unit by using a double 50-gram charge of tungstic oxide contained in two quartz boats arranged one above the other within the reduction tube. Although the quantity of tungsten powder produced approximately doubled with this arrangement, a marked decrease in BET surface area and a corresponding increase in crystallite size occurred. Results are reported in Table 6. The marked decrease in surface area that resulted from the changeover to two boats arranged "piggy back" in the reduction tube has been attributed to the reaction of a larger charge of tungstic oxide with hydrogen to form water vapor, thereby producing a higher partial pressure of water vapor in the hydrogen-reducing gas. As shown by Table 6, particle growth or sintering was more pronounced at the bottom boat location where moisture removal by the incoming hydrogen gas was greatly impeded by the top boat.

A reduction in the surface area of tungsten powder which occurs as a result of promoted sintering action by higher concentrations of water vapor in the hydrogen

Table 5
RELATIONSHIP OF SURFACE AREA WITH FREE FLOW
AND TAP DENSITY OF TUNGSTEN POWDERS

Surface Area (m ² /gm)	Free-Flow Density (gm/cc)	Tap Density (gm/cc)
12.63	0.65	1.10
10.12	1.11	1.45
9.73	0.76	1.45
9.65	0.89	1.65
9.55	1.08	1.50
8.84	0.79	1.33
8.84	1.04	1.43
8.71	0.84	2.18
8.55	0.61	1.39
8.53	0.96	1.54
8.49	0.58	1.44
8.16	1.00	1.43
8.08	0.97	1.43
7.89	0.82	1.57
7.65	0.81	1.26
7.65	0.89	1.50
6.72	1.13	1.53
6.56	1.06	1.49
6.44	1.16	1.57
6.28	1.09	1.50
6.28	1.15	1.53
6.13	0.86	1.39
5.83	0.93	1.50
5.78	0.93	1.74
5.75	1.09	1.46
5.29	0.91	1.55
5.13	1.27	1.64
5.11	1.02	1.40
4.94	1.10	1.54
4.53	2.04	3.08
4.29	2.03	3.17
4.21	1.13	1.79
4.18	1.14	2.13
4.16	1.28	1.88
3.89	1.05	1.9
3.78	1.41	3.15
3.77	1.17	1.81
3.7	1.00	1.73
3.6	2.36	3.40
3.5	0.97	1.67
3.3	2.1	3.2
3.21	1.17	2.73
2.9	1.17	2.05
2.68	1.77	3.54
2.6	1.13	2.14
2.55	1.83	3.20
2.32	1.09	2.70
2.31	1.48	3.36
2.04	2.32	4.16
1.85	2.22	3.90
1.85	2.32	4.13
1.61	1.30	2.87
1.43	1.48	4.00
1.14	1.05	2.29
1.07	2.50	3.74
0.99	2.60	3.74
0.73(1)	2.54	4.68
0.27(2)	3.27	5.10
0.14(3)	2.73	4.00

(1) Company B, Type II commercial powder.

(2) Company A, commercial powder.

(3) Company B, Type I commercial powder.

Table 6
COMPARISON OF THE TUNGSTEN POWDER PRODUCT
FROM TOP AND BOTTOM BOAT POSITIONS

Run Number	Reduction Temperature (° C)	Surface Area (m ² /gm)		Oxygen (%)		Crystallite Size (Å)					
		Top Boat	Bottom Boat	Top Boat	Bottom Boat	Top Boat			Bottom Boat		
						High	Low	Avg	High	Low	Avg
38	700	5.11	3.77	1.20	2.30	431	401	416	582	555	565
39	700	4.94	4.16	1.79	1.38	476	461	469	540	555	524
40	750	2.31	1.43	1.56	1.68	-	-	-	-	-	-
41	800	2.68	2.55	0.25	0.25	524	486	505	582	532	557
42	850	3.78	2.58	0.40	0.23	422	390	386	608	579	593
44	750	4.18	3.21	0.30	0.27	383	360	371	461	436	449
45	750	3.72	2.64	0.48	0.49	467	410	438	595	543	569
46	750	3.49	2.90	0.45	0.44	436	417	426	582	542	562
47(1)	750	3.05	1.51	0.33	0.25	-	-	-	-	-	-
50	750	4.21	1.14	0.51	0.12	414	378	396	740	730	735
53	700	8.84	7.65	1.01	0.92	344	310	327	376	372	374

(1) Tungstic oxide pellets used.

reducing gas is also shown in Table 7. These data were obtained by sampling the tungsten product at various locations in the reduction boat (ie, upstream and downstream) where powder was exposed to relatively low and high concentrations of water vapor, respectively. The tungsten powder located at the inlet end (upstream) also had a much blacker appearance, indicative of higher surface area, compared to that for the outlet end (downstream) of the boat.

Table 7
EFFECT OF WATER VAPOR IN HYDROGEN GAS ON THE TUNGSTEN SURFACE AREA

Weight of WO ₃ (gms)	Hydrogen Gas Flow (l/min)	Reduction Temperature (° C)	Surface Area of Tungsten Product (m ² /gm)		
			Upstream	Middle	Downstream
118	12	700	5.48	5.07	4.93
6(1)	12	700	11.27	7.66	7.56
6(1)	12	700	12.72	10.77	9.04
110	4.4	800	5.42	2.94	1.23
50	12	700	11.23	-	8.12
50	12	700	10.04	7.09	7.75
50	6	700	6.16	5.94	5.81

(1) Pressed into pellets at 38,000 psi.

The effect of a static-bed tungstic oxide reduction on the characteristics of tungsten powder is also shown in Table 8. The powder product resulting from the hydrogen reduction of a 50-gram batch of tungstic oxide which was spread out over a 16-inch length in the quartz reduction boat was divided up with four portions of approximately equal mass. As shown by Table 8, the higher concentration of water vapor at the downstream quartiles resulted in a corresponding decrease in surface area, an increase in oxygen content, and an increase in crystallite size.

Table 8
 VARIATION OF TUNGSTEN POWDER CHARACTERISTICS FROM
 A STATIC-BED REDUCTION OF TUNGSTIC OXIDE
 (50 Gms WO_3 Reduced at 800°C for 4.0 Hours with 9.1 l H_2/Min)

Powder Quartile	Quartile Position in Boat	Surface Area (m^2/gm)	O_2 (%)	Tungsten Powder Product		
				Crystallite Size ($\text{\AA}$)		Avg
				High	Low	
First	Upstream Portion	6.16	1.31	485	252	368
Second	Upstream Middle Portion	5.41	0.44	518	418	468
Third	Downstream Middle Portion	3.50	0.30	545	438	491
Fourth	Downstream Portion	2.08	0.28	582	513	547

To avoid the promotion of particle growth by moist hydrogen during reduction, most experimental reduction runs were conducted with a relatively high flow of hydrogen gas (ie, 12 liters/minute) to sweep away water vapor from the reaction zone as rapidly as possible. Also, the use of the "double boat" arrangement was discontinued.

Effect of Oxide Particle Size - The particle size of the tungstic oxide used in preparing tungsten powder by hydrogen reduction had a pronounced effect upon the surface area (and crystallite size) of the tungsten powder produced. In general, under equivalent reduction conditions, tungstic oxide having a relatively low surface area (ie, $10 \text{ m}^2/\text{gm}$) produced tungsten metal powder having a relatively high surface area, and tungstic oxide having a relatively high surface area (ie, $30 - 50 \text{ m}^2/\text{gm}$) produced tungsten powder having a relatively low surface area. When the surface area was expressed as m^2/cc , the low-surface-area oxides showed an increase in the surface area on reduction, whereas the high-surface-area oxides showed a decrease in the surface area. This effect is shown in Table 9 for a limited number of tungsten oxide batches where surface area data were available.

It is suspected that porosity and the state of aggregation of the oxide and of the tungsten powder product may be complicating factors influencing the results shown in Table 9. The state of aggregation of the oxide would be an important parameter from the standpoint of affecting the bulk density and bed depth of the oxide as contained in the reduction boat and influencing gas permeability and diffusion rates. In consideration of the wide variation in the free-flow and tap density shown in Table 5 for the various tungsten powders prepared by hydrogen reduction of a variety of APT and oxide powders (having surface areas ranging from 2 to $50 \text{ m}^2/\text{gm}$), it is believed that the corresponding oxides used in preparing these tungsten powders also exhibited a wide variation in the bulk density upon being loaded on the quartz reduction boat. Unfortunately, data relating the initial oxide surface area and the bulk density to the surface area and bulk density of the tungsten powder products are not available.

It is believed that, under the static powder-bed reduction conditions employed, moist hydrogen was chiefly responsible for the fine oxide yielding the coarser tungsten powders. Since the mass transfer of tungsten oxide in the presence of water

Table 9
EFFECT OF THE TUNGSTIC OXIDE SURFACE AREA
ON REDUCED TUNGSTEN POWDER

WO ₃		Reduction Temperature(1) (° C)	Tungsten Powder		Average Crystallite Size (Å)
Surface Area (m ² /gm)	(m ² /cc)		Surface Area (m ² /gm)	(m ² /cc)	
1.4(2)	10.0	700	8.1	156	208
1.4(2)	10.0	700	7.9	152	246
2.2(2)	15.7	700	9.7	187	239
2.2(2)	15.7	700	7.1 - 10.0	137 - 193	300
2.2(2)	15.7	850	2.3	44	569
7.9(3)	56.5	700	5.0	97	498
7.9(3)	56.5	700	5.8	112	529
7.9(3)	56.5	700	5.9	114	400
7.9(3)	56.5	700	6.0	116	355
7.9(3)	56.5	700	4.9	95	540
7.9(3)	56.5	800	3.6	70	620
10.9(3)	78	700	9.6	185	191
10.9(3)	78	700	8.1	156	217
10.9(3)	78	700	9.9	190	185
10.9(3)	78	700	8.2	158	252
30.4(3)	218	700	1.7	33	787
30.4(3)	218	700	2.0	39	786
30.4(3)	218	700	2.7	52	1063
30.4(3)	218	700	2.1	41	998
30.4(3)	218	800	2.0	39	853
30.2(4)	216	700	10.1	196	226
30.2(4)	216	700	7.5	145	200
34.1(4)	245	700	8.2	158	253
34.1(4)	245	700	8.1	156	251

(1) 50 grams of tungstic oxide reduced at a specified reduction temperature for 4.0 hours using a hydrogen flow rate of 12 liters/minute.

(2) Prepared by oxidizing commercial tungsten powder (Company B, Type I) at 500° C.

(3) Prepared by wet chemical precipitation in the laboratory.

(4) Prepared by wet chemical precipitation in pilot-plant-scale quantities (ie, ~ 100 lbs).

vapor from one part of a powder bed to another has been established,⁽¹⁸⁾ sublimation of the oxide and gas plating of metal on metal surfaces may be the mechanism associated with particle coarsening.

Properties of Freshly Reduced Powders

Pyrophoricity and Hygroscopicity - Hydrogen reduction of tungstic oxide powders at 700° C gave pyrophoric tungsten metal powders even after extensive purging with nitrogen or helium to remove occluded hydrogen. It was subsequently found that the application of a suitable vacuum (ie, ~ < 10 μ Hg) to the freshly reduced tungsten powder, prior to exposure to air, greatly reduced its potential pyrophoricity. The

slow admittance of air (~ 0.5 hr) to the reduction tube (after suitable vacuum treatment had been applied) was also effective in reducing potential pyrophoricity of freshly reduced powders. It is believed that the slow formation of a surface oxide film in this manner, which dissipates the heat of oxidation, provides some stabilization against further oxidation. If the oxide film is allowed to form too rapidly, however, pyrophoricity of the powder will result.

In a systematic study of the controlled oxidation of polished tungsten specimens at high temperature, Gulbransen⁽¹⁹⁾ showed that the oxidation of tungsten started with the adsorption of a layer of oxygen on the surface and the rapid formation of a thin oxide film. This action was followed by the growth of the oxide from crystallization nuclei such that thicker films were nonuniform.

The extent of surface oxidation of a static bed of freshly reduced tungsten metal powder exposed to air at room temperature is shown in Figure 22. After a 24-hour exposure period, an overall gain in weight of approximately one percent was noted for three square inches of exposed surface. Although some loss in weight resulted from vacuum drying these samples at 75°C , the samples failed to return to their original weights, indicating both moisture and oxygen pickup. Of the total one percent cumulative weight gain, it is estimated that 0.8% may be attributed to oxidation and 0.2% to the adsorption of moisture from the atmosphere.

Figure 22. SURFACE OXIDATION OF FRESHLY REDUCED TUNGSTEN POWDER AT ROOM TEMPERATURE. (Two Different Portions of the Batch; $SA \sim 9.5 \text{ m}^2/\text{gm}$)

Oxygen Pickup During Compaction - A study was made of the extent of oxygen pick-up on tungsten powder which occurs from exposure to air upon loading the powder into pellet molds prior to isostatic compaction. Oxygen analyses of various batches of tungsten powder, sampled immediately after reduction and subsequently upon extensive exposure to air after completing the pellet-loading operations, are shown in Table 10. These data show significant increases in the oxygen content ranging from approximately 10 to 75% over that of the initial oxygen content. The extent of the oxygen pickup also appears to be dependent upon the surface area of the tungsten powder. Where sufficient powder sample has been available, surface-area analyses after pellet loading are included and show a slight decrease after air exposure.

Table 10
OXYGEN PICKUP OF TUNGSTEN POWDER RESULTING FROM EXPOSURE
TO AIR DURING PELLET-LOADING OPERATIONS

Before Pellet Loading		After Pellet Loading		Relative Percent O ₂ Change
Surface Area (m ² /gm)	Percent O ₂	Surface Area (m ² /gm)	Percent O ₂	
8.55	1.86	-	3.28	76.5
-	1.03	-	1.78	72.8
8.73	1.60	8.71	2.35	41.8
8.08	1.72	7.87	2.40	39.5
3.58	0.44	-	0.54	23.7
-	0.50	-	0.61	22.0
9.73	2.34	9.10	2.74	17.1
8.07	1.79	6.59	1.95	8.5
3.81	0.61	3.40	0.66	8.2

Several batches of tungsten powder have been handled completely in an inert atmosphere using an inert-atmosphere glove box for unloading the batch from the reduction tube, sampling, and loading the powder into sealed latex finger cost for isostatic pressing. Despite these precautions, several powder compacts burned upon subsequent exposure to air after pressing at 30,000 psi.

Relationship of Oxygen Content and Surface Area - After several batches of high-surface-area tungsten powder (5 - 10 m²/gm) had been prepared, it was observed that the oxygen content of these powders was correspondingly high (~1.0 - 1.5%). A general relationship between the surface area and the oxygen content of laboratory-prepared tungsten powders was found to exist, as shown in Figure 23. The oxygen content of several commercial powders is also shown for comparison.

Relationship of Nitrogen and Oxygen Content - As shown by Figure 24, the nitrogen content of the tungsten powder batches produced in this laboratory appears to be related to the oxygen content of the powder. It is suspected that both the nitrogen and oxygen pickup result from initial exposure of the freshly prepared powder to air. In general, the higher the surface area of the powder the greater the oxygen and nitrogen pickup because of the increased reactivity of high-surface-area powders.

Figure 23. OXYGEN CONTENT AS A FUNCTION OF THE SURFACE AREA OF TUNGSTEN POWDER.

Deviations from this general relationship were found for a few batches of high-surface-area tungsten powders that had been exposed to air too rapidly. For these powders, excessive oxidation of the tungsten particles occurred, as was evident by the batch becoming mildly warm but not warm enough to initiate active burning. This reaction and heating resulted in a decrease of the surface area of the powder.

Relationship of Surface Area and Green Compact Density - The general relationship between the surface area of the tungsten powder and its green (pressed) compact density is plotted in Figure 25. The data points shown for laboratory-prepared powders were obtained during the initial phases of this investigation by die pressing the tungsten compacts. The powders were prepressed at 10,000 psi, ground by a mortar and pestle, screened through a 40-mesh sieve, and the minus 40-mesh fraction was repressed at 30,000 psi. The density of these compacts (~ 0.5 -inch OD $\times$ 0.5-inch

Figure 24. RELATIONSHIP BETWEEN THE OXYGEN AND NITROGEN CONTENTS OF LABORATORY-PREPARED TUNGSTEN POWDERS.

L) was computed after weighing in air and obtaining the volume of the compact from caliper measurement of its physical dimensions.

It was also observed that although the ultra-fine laboratory-prepared powders showed the lowest green densities after compaction at 30,000 psi, these powders exhibited the highest amount of shrinkage and densification after sintering. The degree of shrinkage and densification resulting from sintering compacts prepared from commercial and laboratory-prepared tungsten powders are discussed in the section entitled, "Shrinkage and Densification", Page 70.

Removal of Carbon from Tungstic Oxide

The presence of carbon as an impurity in finely divided tungsten metal powder was suspected to have a detrimental effect on the sinterability and mechanical properties of tungsten powder compacts since it might constitute an interfering phase and reduce the cohesion between particles. A study was made on the effectiveness of air oxidation as a method of removing carbon from tungstic oxide prior to reduction.

A 100-gram batch of tungstic oxide which had been spiked with 0.6% carbon (as lamp black) was distributed into small Alundum boats (~1/4" bed depth) and placed in a muffle furnace maintained at 500° C and provided with a small air bleed. Periodic removal of the tungstic oxide samples in triplicate for carbon analysis

Figure 25. CORRELATION BETWEEN THE GREEN COMPACT DENSITY AND THE TUNGSTEN POWDER SURFACE AREA.

showed that the carbon content had been reduced to less than 50 ppm within seven hours. Results are plotted in Figure 26 in which each datum point represents an average of three carbon determinations.

The initial surface area of the tungstic oxide was 30.4 m²/gm. After 3.0 and 7.0 hours in the muffle furnace, the surface area of the tungstic oxide had decreased to 15.3 and 14.5 m²/gm, respectively. Thus, the employment of an excessive calcination temperature with tungstic oxide may have a detrimental effect upon the particle size of the oxide produced.

Removal of Carbon from Tungsten Powder

A large batch of commercial tungsten powder (Company A) was spiked with 0.5% carbon (as lamp black), and 25-gram portions of this loose carbon-spiked powder contained in Alundum boats were sintered for 3.0 hours in flowing, dry, purified hydrogen gas at various temperatures. Results, shown in Figure 27, indicate that carbon is readily removed from tungsten powder at elevated temperatures (ie, 1000° C), probably as a volatile hydrocarbon product, and that finely divided tungsten may serve as a catalyst for this reaction. Each datum point shown in this figure represents an average of four individual carbon determinations.

Figure 26. REMOVAL OF CARBON FROM TUNGSTEN OXIDE BY AIR OXIDATION AT 500°C.

According to Mantell, (20) there is no reaction between carbon and hydrogen at ordinary temperatures. At temperatures in the range from 1100 to 1500° C a small amount of methane is formed. This reaction is accelerated by platinum as a catalyst. When nickel is used as a catalyst, the reaction proceeds at temperatures in the neighborhood of 500° C.

Sinterability

Effect of Time at the Sintering Temperature - A study was made to determine the effect of the hold time at the sintering temperature of 1500° C on density, using a flowing hydrogen atmosphere. For these studies, compacts were pressed isostatically at 30,000 psi from a batch of laboratory-prepared tungsten powder having a medium surface area of 5.6 m²/gm and an oxygen content of 1.1%.

Figure 27. EFFECT OF TEMPERATURE ON THE CARBON-SPIKED COMMERCIAL TUNGSTEN POWDER IN A FLOWING HYDROGEN ATMOSPHERE. (Hold Time - 3.0 Hours)

Results, as plotted in Figure 28, indicate that only a very negligible increase in the sintered density occurs beyond the 3.0-hour hold time arbitrary standard chosen for evaluating the density of sintered tungsten compacts in this investigation. As also shown by Figure 28, an increase in the density was realized from approximately 89% of the theoretical density after a three-hour hold time to approximately 91% of theoretical after nine hours. Each density datum point shown in this figure represents the average density of three or four compacts.

Effect of the Reduction Temperature and Moisture Removal - Several hundred tungsten powder compacts have been prepared from laboratory batches of tungsten powder by isostatically pressing and sintering. The pellets were sintered for 3.0 hours at 1500° C in a flowing hydrogen atmosphere in the furnace described previously (Figure 9). A partial listing of some typical sintered densities obtained from various types of tungstic oxide is given in Table 11. For comparison, a compilation of the sintered densities obtained for four types of typical, very-fine, commercially available tungsten powders is given in Table 12.

Figure 28. EFFECT OF THE SOAK TIME AT A 1500° C SINTERING TEMPERATURE ON THE DENSITY OF TUNGSTEN COMPACTS PRESSED AT 30,000 PSI.

These results show a wide variation in the sintered density according to the method of preparation of the tungsten compound from which the metal was produced. The highest sintered pellet densities (94 - 98% of theoretical) were obtained from tungstic oxide produced by wet chemical techniques and reduced at 700° C with a large excess of hydrogen gas. When this material was reduced at 800 to 850° C under otherwise identical reduction conditions, sintered densities were depressed to only approximately 70% of theoretical.

Sintered compact densities were also depressed by using an insufficient hydrogen flow rate during the reduction of the tungstic oxide as a result of promoted sintering by the presence of moisture. An inspection of Table 11 which lists several batches of tungsten powder reduced simultaneously in boats arranged "piggy back" within the reduction tube shows that the tungsten compacts prepared from powder in the top boat consistently gave higher sintered densities than compacts prepared from powder in the bottom boat where moisture removal was impeded by the physical presence of the top boat.

The adverse effect of increasing the reduction temperature on sinterability and surface area, as was discussed earlier, is indicated in Table 13. Reduction of tungstic oxide at 700 and 850° C under otherwise equivalent conditions gave sintered compact densities of 92 and 73%, respectively.

Table 11

SINTERABILITY OF TUNGSTEN PREPARED BY THE HYDROGEN REDUCTION OF TUNGSTIC OXIDE
(Arranged According to the Hydrogen Flow Rate)

Type WO ₃ (1)	Batch Number	Type Boat(2)	Reduction Conditions				Tungsten Powder			Sintered Pellet Density(3)	
			Charge (gms)	Time (hrs)	Temperature (° C)	H ₂ Flow (l/min)	Surface Area (m ² /gm)	Area (m ² /cc)	Percent O ₂	(gm/cc)	(% TD)
WC	L-16	S	50	4	700	12	10.1	196	1.70	18.3	94.9
WC	L-16	S	50	4	700	12	10.1	196	1.70	18.3	95.0
WC	L-16	S	50	4	700	12	10.1	196	1.70	18.3	95.0
WC	L-16	S	50	4	700	12	10.1	196	1.70	18.3	95.0
WC	W-49	S	118	4	700	12	5.2	101	1.06	18.9	98.1
WC	W-49	S	118	4	700	12	5.2	101	1.06	18.9	98.1
WC	W-53	T	62	6	700	12	8.8	171	1.01	18.3	94.8
WC	W-53	T	62	6	700	12	8.8	171	1.01	18.1	93.7
WC	W-53	T	62	6	700	12	8.8	171	1.01	17.7	91.7
WC	W-53	T	62	6	700	12	8.8	171	1.01	18.0	93.3
WC	W-53	B	26	6	700	12	7.6	148	0.92	17.9	92.7
WC	W-57	S	50	4	700	12	1.7	33	0.24	18.6	96.3
WC	W-57	S	50	4	700	12	1.7	33	0.24	18.6	96.2
WC	W-57	S	50	4	700	12	1.7	33	0.24	18.6	96.1
WC	W-57	S	50	2(4)	700	12	2.0	38	0.58	18.6	96.2
WC	W-57	S	50	2(4)	700	12	2.0	38	0.58	18.7	96.8
WC	W-57	S	50	2(4)	700	12	2.0	38	0.58	18.7	97.0
APT	W-55	S	50	4	700	12	8.9	173	1.98	12.0	62.3
APT	W-55	S	50	4	700	12	8.9	173	1.98	11.1	57.4
IE	W-50	S	70	4	700	9.8	-	-	-	18.5	95.7
IE	W-50	S	70	4	700	9.8	-	-	-	18.7	97.0
IE	W-50	S	70	4	700	9.8	-	-	-	18.1	93.6
IE	W-50	S	70	4	700	9.8	-	-	-	18.7	97.1
IE	W-50	S	70	4	700	9.8	-	-	-	18.6	96.5
IE	W-50	S	70	4	700	9.8	-	-	-	18.3	94.8
WC	W-52	T	25	2	700	8.9	12.6	244	1.63	18.1	93.8
WC	W-52	T	25	2	700	8.9	12.6	244	1.63	18.2	94.2
WC	W-52	B	75	6	700	8.9	8.5	164	0.86	18.1	93.8
WC	W-52	B	75	6	700	8.9	8.5	164	0.86	18.1	94.0
WC	W-52	B	75	6	700	8.9	8.5	164	0.86	18.2	94.3
WC	W-52	B	75	6	700	8.9	8.5	164	0.86	18.2	94.5
WC	W-52	B	75	6	700	8.9	8.5	164	0.86	17.5	90.8
WC	W-52	B	75	6	700	8.9	8.5	164	0.86	18.0	93.2
WC	W-51	S	50	4	700	6	5.1	99	0.87	18.7	96.8
WC	W-51	S	50	4	700	6	5.1	99	0.87	18.9	98.0
WC	W-51	S	50	4	700	6	5.1	99	0.87	18.9	97.9
WC	W-51	T	75	16	700	6	5.9	113	0.74	18.7	96.8
WC	W-51	T	75	16	700	6	5.9	113	0.74	18.7	96.9
WC	W-51	T	75	16	700	6	5.9	113	0.74	18.7	97.1
WC	W-51	T	75	16	700	6	5.9	113	0.74	18.6	96.5

(1) WC = WO₃ prepared by wet chemical precipitation.

IE = WO₃ prepared by ion exchange.

APT = Ammonium paratungstate, fine crystals.

OX = WO₃ from oxidized commercial tungsten powder (Company B, Type II).

(2) T = Top Boat

B = Bottom Boat

S = Single Boat

(3) Sintered three hours at 1500° C in purified hydrogen.

(4) Intermittent evacuation applied during reduction to facilitate moisture removal.

Table 11 (Continued)

Type WO ₃ (1)	Batch Number	Type Boat(2)	Reduction Conditions				Tungsten Powder		Percent O ₂	Sintered Pellet Density ⁽³⁾	
			Charge (gms)	Time (hrs)	Temperature (° C)	H ₂ Flow (l/min)	Surface Area (m ² /gm)	(m ² /cc)		(gm/cc)	(% TD)
WC	W-51	T	75	16	700	6	5.9	113	0.74	18.8	97.2
WC	W-51	T	75	16	700	6	5.9	113	0.74	18.4	95.1
WC	W-51	T	75	16	700	6	5.9	113	0.74	18.7	96.7
WC	W-51	B	70	16	700	6	5.0	98	0.57	17.4	90.0
WC	W-51	B	70	16	700	6	5.0	98	0.57	17.4	90.2
WC	W-51	B	70	16	700	6	5.0	98	0.57	17.1	88.6
WC	W-51	B	70	16	700	6	5.0	98	0.57	16.6	86.0
OX	-	S	60	4	700	6	4.7	90	1.90	18.6	96.6
OX	W-51	S	60	4	700	6	4.7	90	1.90	18.4	95.7
WC	W-40	T	40	12	700	6	4.9	95	1.79	18.8	97.5
WC	W-40	T	40	12	700	6	4.9	95	1.79	18.7	96.7
WC	W-40	B	40	12	700	6	4.2	80	1.38	18.4	95.2
WC	W-40	B	40	12	700	6	4.2	80	1.38	18.3	94.9
IE	W-50	T	80	6	750	4.4	4.2	81	0.51	17.5	90.5
IE	W-50	T	80	6	750	4.4	4.2	81	0.51	15.7	81.4
IE	W-50	T	80	6	750	4.4	4.2	81	0.51	17.4	90.1
IE	W-50	T	80	6	750	4.4	4.2	81	0.51	17.8	92.3
IE	W-50	T	80	6	750	4.4	4.2	81	0.51	16.3	84.7
IE	W-50	T	80	6	750	4.4	4.2	81	0.51	17.1	88.9
IE	W-50	B	80	6	750	4.4	1.1	22	0.12	13.0	67.3
IE	W-50	B	80	6	750	4.4	1.1	22	0.12	14.7	76.3
IE	W-50	B	80	6	750	4.4	1.1	22	0.12	14.7	75.9
IE	W-48	T	40	4	750	4.4	3.5	67	0.45	17.3	89.5
IE	W-48	T	40	4	750	4.4	3.5	67	0.45	16.3	84.6
IE	W-48	B	40	4	750	4.4	2.9	56	0.44	16.6	85.9
IE	W-48	B	40	4	750	4.4	2.9	56	0.44	16.5	85.5
WC	W-40	T	40	6	800	4.4	2.7	52	0.25	14.0	72.8
WC	W-40	B	40	6	800	4.4	2.6	49	0.25	13.5	69.8
WC	W-40	T	32	6	850	4.4	3.8	73	0.40	14.2	73.8
WC	W-40	T	32	6	850	4.4	3.8	73	0.40	13.8	71.6
WC	W-40	B	40	6	850	4.4	2.6	50	0.23	12.8	66.2
IE	W-47	T	40	8	750	4.4	3.7	72	0.48	17.6	91.1
IE	W-47	T	40	8	750	4.4	3.7	72	0.48	16.8	86.8
IE	W-47	B	40	8	750	4.4	2.6	51	0.49	16.9	87.5
IE	W-47	B	40	8	750	4.4	2.6	51	0.49	17.1	88.5
WC	W-34	S	28	4	750	4.4	5.8	111	1.14	16.4	84.8

(1) WC = WO₃ prepared by wet chemical precipitation.IE = WO₃ prepared by ion exchange.

APT = Ammonium paratungstate, fine crystals.

OX = WO₃ from oxidized commercial tungsten powder (Company B, Type II).

(2) T = Top Boat

B = Bottom Boat

S = Single Boat

(3) Sintered three hours at 1500° C in purified hydrogen.

(4) Intermittent evacuation applied during reduction to facilitate moisture removal.

Effect of the Forming Pressure - The effect of pressure used in forming the tungsten compacts isostatically is another variable affecting the sintered density. A plot of the sintered density as a function of the isostatic forming pressure for various batches

Table 12
SINTERABILITY OF TYPICAL COMMERCIAL TUNGSTEN POWDERS
(3.0 Hours at 1500° C in Flowing Hydrogen)

Type Powder	Surface Area (m ² /gm)	Percent O ₂	Average Crystallite Size (Å)	Sintered Density	
				(gm/cc)	(% TD)
Company B, Type II	0.7	0.3	1018	16.2	84.1
				15.9	82.3
				16.6	85.9
				16.1	83.5
				16.4	85.3
				15.1	78.0
				15.4	80.0
				16.6	86.1
Company B, Type I	0.14	0.09	2375	16.4	85.0
				12.2	63.3
				12.2	63.1
Company A	0.27	0.06	1693	12.2	63.2
				12.5	64.7
				12.8	66.1
Company C	14.9	1.3	234	12.6	65.5
				16.9	87.3
				16.4	85.1
				16.8	86.9

of laboratory-prepared tungsten powder representing different tungstic oxide types is presented in Figure 29. The batch prepared from the oxide obtained by wet chemical precipitation did not show any appreciable change in the sintered density with forming pressures from 10,000 to 38,000 psi, while the others did; thus, the results of the pressing technique may be altered considerably by differences in particle size or agglomerate structure.

A plot of the sintered density as a function of the isostatic forming pressure for a batch of commercial tungsten powder (Company A) and a batch of tungsten powder made from oxidized commercial powder (Company B, Type II) under laboratory reduction conditions is also presented in Figure 29. These data show that the density of sintered tungsten compacts increases with increasing applied compacting pressures up to 40,000 psi.

The general increase in the sintered density that was obtained by increased isostatic compaction pressures may be attributed to the rupturing of the particle surface films by abrasion and improved contact because of greater particle deformation. Although a slight increase in the sintered density occurred from 30,000 to 40,000 psi, the use of 30,000 psi appears to be a practical limit for the formation of production-scale tungsten bodies at Y-12.

Effect of High-Pressure Compaction - Several small compacts were made from a typical commercial powder (Company B, Type I) and a batch of laboratory-prepared

Table 13
EFFECT OF THE REDUCTION TEMPERATURE ON SINTERABILITY

Reduction Conditions			Surface Area		Sintered Density	
Charge (gms)	Time (hrs)	Temperature (° C)	(m ² /gm)	(m ² /cc)	(gms/cc)	(% TD)
Tungstic Oxide from APT ⁽¹⁾						
50	5.5	700	9.5	183	17.8	92.1
50	6.0	750	5.7	110	16.9	87.3
50	6.0	800	3.6	70	15.9	82.3
50	6.0	850	2.0	39	14.1	72.9
Tungstic Oxide from Wet Chemical Precipitation						
40T ⁽²⁾	12.0	700	4.9	95	18.8	97.5
					18.7	96.5
40S	4.4	750	6.7	129	18.2	94.3
					18.2	94.2
					18.5	96.0
40T	6.0	800	2.7	52	14.0	72.8
32T	6.0	850	3.8	74	14.2	73.8
					13.8	71.6
40B	12.0	700	4.2	81	18.4	95.2
					18.3	94.9
40B	6.0	800	2.6	50	13.5	69.8
40B	6.0	850	2.6	50	12.8	66.2

(1) Commercial APT from Company D.

(2) T = Top Boat Position

B = Bottom Boat Position

S = Single Boat-Used

powder of medium surface area (6 m²/gm) by isostatic pressing in special dies at pressures up to 200,000 psi. At 200,000 psi, the green density of the compact made from commercial powder was 15.4 gms/cc or approximately 80% of the theoretical density, but the green density of the compact made from laboratory-prepared powder was only 11.0 gms/cc, or approximately 57% of the theoretical density.

After presoaking these pellets in a flowing, purified hydrogen atmosphere for 2.0 hours at 600° C, 2.0 hours at 800° C, and sintering for 3.0 hours at 1500° C, the laboratory compact showed a density of 17.9 gms/cc or 93% of theoretical, whereas the commercial compact showed a density of 16.1 gms/cc or approximately 83.5% of theoretical—a very insignificant gain in densification over that of its green density. Comparative results at other compaction pressures are shown in Figure 30. These studies indicate that the commercial powder was highly compactable under high pressure, but that it was not very sinterable despite the high compacting pressures employed.

Effect of Oxygen - The oxygen content of tungsten powder has a pronounced effect on the sintering properties of pressed metal compacts, as shown in Table 14. These

Figure 29. EFFECT OF THE ISOSTATIC FORMING PRESSURE ON THE SINTERED DENSITY. (3.0 Hours at 1500°C in Hydrogen)

data, representing various batches of laboratory-prepared tungsten powder reduced at 650 - 700° C under otherwise equivalent conditions, are arranged according to the increasing oxygen content for each tungstic oxide batch. The decrease in the sintered density with increasing oxygen content is quite apparent.

According to Goetzel,⁽¹⁴⁾ tungsten powder does not sinter very easily if absolutely free of oxygen, especially if the oxide is present in the form of thin envelopes around the particles. It is apparent from Table 14, however, that a high oxygen content (ie, > 1% O₂) has a very deleterious effect on sinterability.

Oxygen Release During Sintering - It is believed that at some stage during the sintering treatment, when the tungsten compacts made from these "high oxygen" powders are heated from room temperature to 1500° C, adsorbed gases are released and some reduction of particle surface oxide films occurs by the diffusion of hydrogen through the compact with the subsequent release of the water vapor that was formed as a result of a chemical reaction. It is suspected that after reaching the temperature at which the shrinkage of the compact becomes pronounced, these reduced gases cannot escape rapidly enough and are trapped within the interior of the compact and form a high internal gas pressure. At some temperature during the heating up or sintering cycle at 1500° C these gases are released with such violence that blowholes, fissures, and even transverse cracking of the compact occurs. The severity and varied

Figure 30. SINTERABILITY OF COMMERCIAL AND LABORATORY-PREPARED TUNGSTEN POWDER COMPACTS AFTER HIGH-PRESSURE COMPACTION.

nature of these surface irregularities on the sintered tungsten compacts made with laboratory-prepared powders containing greater than 1% oxygen are shown in Figure 31.

Effect of Prereduction with Hydrogen - The effect of prereducing tungsten compacts containing relatively high oxygen contents in a flowing hydrogen atmosphere at intermediate temperatures (600 and 800° C prior to sintering at 1500° C) was studied. It was believed that such a prereduction treatment would allow the adsorbed gases and gaseous products of the reaction of hydrogen with the oxide film to escape from the interior of the compact before the interpore channels became sealed at the temperature of sintering and shrinkage. Results, as summarized in Table 15, indicate that a substantial increase in the sintered density may be realized by prereducing the powder in hydrogen at 800° C.

Prereduction for four hours at 600° C appeared to be relatively ineffective. The sintered densities shown in Table 15 represent an average of three determinations (ie, three compacts) in most cases. These prereduction tests are

Table 14
EFFECT OF THE OXYGEN CONTENT OF TUNGSTEN POWDER ON THE SINTERED PELLET DENSITY
(H₂ Flow Rate During Reduction Was 12 Liters/Minute)

Batch Number	WO ₃ Surface Area (m ² /gm)	Reduction Temperature (° C)	Tungsten Powder		Percent O ₂	Average Crystallite Size (Å)	Sintered Pellet Density ⁽²⁾	
			Surface Area (m ² /gm)	Surface Area (m ² /cc)			(gms/cc)	(% TD)
L-16 ⁽¹⁾	30.3	700	10.1	196	1.70	226	18.3	94.9
							18.3	95.0
							18.3	95.0
							18.3	95.0
L-16	30.3	700	7.5	145	1.82	200	17.7	91.8
							18.1	93.9
							18.2	94.3
							17.8	92.2
L-16	30.3	650	15.6	301	3.05	156	17.8	92.4
							17.9	92.5
L-16	30.3	650	13.8	266	3.70	142	17.3	89.7
							17.3	89.6
							16.9	87.5
							16.8	86.8
L-31	34.1	700	8.1	155	1.79	251	17.5	90.6
							18.3	95.0
							18.2	94.1
							18.2	94.1
L-31	34.1	700	8.2	158	2.68	253	17.6	91.1
							17.6	90.7
							17.4	90.4
							17.4	90.4
L-31	34.1	600	17.6	340	5.41	136	16.5	85.3
							16.5	85.3
							15.9	82.2
							16.0	83.1
W-62	10.9	700	8.1	156	1.72	217	18.8	96.9
							18.6	96.3
W-62	10.9	700	9.6	185	1.98	191	15.9	82.2 ⁽³⁾
							18.0	93.1
							18.1	93.7
W-62	10.9	700	9.9	190	3.18	185	16.9	87.4
							16.7	86.5
							16.9	87.4
							17.3	89.7
W-62	10.9	700	8.2	158	3.92	252	17.0	87.9
							16.7	86.7
							16.8	86.9
							16.7	86.6
W-56	7.9	700	5.8	112	0.83	529	18.3	95.0
							18.4	95.5
							18.3	94.9
							18.5	95.8
W-56	7.9	700	-	-	1.03	540	18.2	94.1
							18.2	94.2
							18.2	94.5
							18.2	94.4

(1) All batches were wet-chemical-precipitated WO₃.

(2) Pellets were pressed isostatically at 30,000 psi and sintered for three hours at 1500° C in H₂.

(3) Suspect pellet became contaminated with oil during pressing.

(4) Reduced with a hydrogen flow of six liters/minute.

(5) Intermittent vacuum applied during reduction.

Table 14 (Continued)

Batch Number	WO ₃ Surface Area (m ² /gm)	Reduction Temperature (° C)	Tungsten Powder		Percent O ₂	Average Crystallite Size (Å)	Sintered Pellet Density ⁽²⁾	
			Surface Area (m ² /gm)	Surface Area (m ² /cc)			(gms/cc)	(% TD)
W-56	7.9	650	-	-	1.31	642	18.5	95.9
							18.4	95.4
							18.5	96.0
W-56	7.9	700	8.5	164	1.56	509	17.4	90.2
							17.6	90.9
							16.5	85.4
W-56	7.9	700(4)	5.9	114	2.04	400	16.3	84.5
							16.2	84.0
							16.3	83.6
							16.0	82.9
							15.8	81.8
W-57	30.4	700	1.7	33	0.24	787	18.6	96.3
							18.6	96.3
							18.6	96.3
W-57	30.4	700	2.7	52	0.41	1063	18.2	94.4
							18.2	94.2
							18.3	95.0
W-57	30.4	700	-	-	0.50	938	18.5	95.9
							18.2	94.2
							18.2	94.2
W-57	30.4	700(5)	2.0	38	0.58	786	18.6	96.2
							18.7	96.8
							18.7	97.0
W-57	30.4	700(5)	3.8	73	0.61	903	18.3	94.6
							18.1	94.0
W-57	30.4	700(5)	2.1	40	0.68	998	18.5	95.9
							18.4	95.1

(1) All batches were wet-chemical-precipitated WO₃.

(2) Pellets were pressed isostatically at 30,000 psi and sintered for three hours at 1500° C in H₂.

(3) Suspect pellet became contaminated with oil during pressing.

(4) Reduced with a hydrogen flow of six liters/minute.

(5) Intermittent vacuum applied during reduction.

largely exploratory and the optimum temperature and time of prereduction treatment have not been established.

The effect of using moist hydrogen gas (ie, approximately 2 ppm H₂O) is shown by the results of Run G in Table 15. Moist hydrogen was obtained by passing cylinder hydrogen gas through a Deoxo unit and then into the sintering furnace, bypassing the Drierite and Molecular Sieve traps and hot titanium sponge bed usually employed. Although some improvement in the sintered density was realized, the time cycle employed for heating to the sintering temperature of 1500° C for this run was approximately one hour longer than usual, and this may have been tantamount to a prereduction treatment.

Effect of Nitrogen -

Preparation of Tungsten Nitride - In the evaluation of the sinterability and mechanical properties of high-purity tungsten and tungsten alloys, information

6X

Pellet X-8

Size - $3/8 \times 5/16$ inch
 Powder Surface Area - $5.6 \text{ m}^2/\text{gm}$
 Powder Oxygen Content - 1.10%

6X

Pellet 56A

Size - $1/4 \times 5/16$ inch
 Powder Surface Area - $17.6 \text{ m}^2/\text{gm}$
 Powder Oxygen Content - 5.41%

6X

Pellet Z-8

Size - $3/8 \times 5/16$ inch
 Powder Surface Area - $6.5 \text{ m}^2/\text{gm}$
 Powder Oxygen Content - 3.36%

10X

Rod X-11

Size - $1/4$ inch D
 Powder Surface Area - $5.6 \text{ m}^2/\text{gm}$
 Powder Oxygen Content - 1.10%

Figure 31. SURFACE IRREGULARITIES OF SINTERED TUNGSTEN COMPACTS HAVING A HIGH OXIDE CONTENT.

Table 15
EFFECT OF A PREREDUCTION TREATMENT ON THE SINTERED DENSITY

Batch Number	Percent O ₂	Sintered Density(1) No Prereduction	Percent of Theoretical Density After Prereduction	Incremental Density Increase Due to Prereduction		
<u>Run A - 2.0 hours at 800° C</u>						
A59	2.18	85.0	92.1	8.4		
A18	1.16	87.0	93.8	7.8		
A48	2.67	85.2	90.3	6.0		
A55	1.56	85.0	89.8	5.6		
A54	1.82	93.1	96.6	3.8		
A45	3.70	88.4	90.8	2.7		
A36	1.52	91.4	93.5	2.3		
A51	2.68	90.6	92.3	1.9		
A49	1.56	90.5	92.0	1.7		
A33	2.00	88.5	89.5	1.0		
<u>Run B - 4.0 hours at 800° C(2)</u>						
X	1.10	87.9	91.3	3.9		
Y	2.27	86.7	89.3	3.0		
Z	3.36	80.4	86.0	7.0		
<u>Run C - 8.0 hours at 800° C</u>						
X	1.10	87.9	92.2	4.9		
Y	2.27	86.7	88.0	1.5		
Z	3.36	80.4	85.5	6.3		
<u>Runs D and E - 22 hours at 800° C</u>						
			<u>Run D</u>	<u>Run E</u>	<u>Run D</u>	<u>Run E</u>
X	1.10	87.9	92.2	91.8	4.9	4.4
Y	2.27	86.7	88.0	88.9	1.5	2.5
Z	3.36	80.4	85.5	85.1	6.3	5.8
<u>Run F - 4 hours at 600° C</u>						
X	1.10	87.9	87.6	0.0		
Y	2.27	86.7	85.3	-1.6		
Z	3.36	80.4	82.0	2.0		
<u>Run G - Moist Hydrogen</u>						
X	1.10	87.9	93.1(3)	5.9		
Y	2.27	86.7	89.7(3)	3.5		
Z	3.36	80.4	85.8(3)	6.7		

(1) Sintered for 3.0 hours at 1500° C in H₂.

(2) Furnace failure at 1400° C upon heating to the sinter temperature; second heating cycle to 1500° C required.

(3) Moist hydrogen used instead of prereduction treatment.

was needed on the effect of nitrogen as an impurity. In studying this effect, several attempts were made to prepare tungsten nitride by the reaction of sub-micron tungsten powder with nitrogen gas and ammonia at various temperatures. The results of these nitriding experiments are summarized in Table 16.

Table 16
PREPARATION OF TUNGSTEN NITRIDE

Run Number	Initial Material(1)	Heating Schedule				Vacuum Applied	Product Analysis		
		Atmosphere	Flow Rate (l/min)	Temperature (° C)	Hold Time (hrs)		Nitrogen (ppm)	Oxygen (%)	Surface Area (m ² /gm)
N-10	Tungsten Powder(2)	Nitrogen	1.6	200	22	Yes	257	1.42	4.83
N-12	Tungsten Powder(2)	Nitrogen	1.6	700	4	Yes	215	1.69	4.52
N-1	Tungsten Powder(2)	Nitrogen	2.4	800	1.0	Yes	174	-	-
N-2	Tungsten Powder(2)	Nitrogen	2.4	975	1.5	No	131	1.18	-
N-5	Tungsten Powder(2)	Nitrogen	-	1500	10	No	108	0.45	0.09
N-11	Tungsten Powder(2)	Ammonia	-	700	4	No	2713	0.80	4.89
N-9	Tungsten Powder(2)	Ammonia	-	200	4	Yes	1474	1.50	4.08
N-4	WO ₃ (3)	Hydrogen	12.0	20 - 700	4	Yes	1790	1.66	10.54
		N ₂ + H ₂	1.6 + 12.0	700	2				
N-8	WO ₃	Hydrogen	12.0	20 - 700	4	Yes	672	1.68	8.82
		Nitrogen	2.4	700	24	Yes			
N-6	WO ₃	Hydrogen	12.0	20 - 700	4	Yes	604	1.71	7.67
		Nitrogen	3.2	700	2	Yes			
N-7(4)	WO ₃	Hydrogen	12.0	20 - 700	4	No	550	1.37	7.24
		Nitrogen	2.4	700	24	No			
N-3	WO ₃	N ₂ + H ₂	1.6 + 9.0	20 - 900	0.8	No	242	0.09	0.95
		N ₂ + H ₂	1.6 + 9.0	900	3	No			
		Nitrogen	3.2	900 - 20	0.8	No			
		Nitrogen	1.6	20	16	No			

(1) Weight: 50 grams.

(2) Analysis: 184 ppm N; 1.10% O₂.

(3) Prepared by wet-chemical precipitation; surface area = 24.4 m²/gm.

(4) Product pyrophoric upon exposure to air; inlet end sample saved before pyrophoricity spread throughout the entire product.

These data show that although ammonia was more effective than nitrogen in increasing the nitride content of tungsten powder, neither treatment accomplished any appreciable conversion to tungsten nitride; ie, WN_2 (13.2% N) or W_2N (3.67% N). As shown in Table 16, several attempts were made to nitride a more reactive tungsten powder freshly reduced from tungstic oxide with hydrogen. Despite the formation of such reactive powders having surface areas as high as $10.5 \text{ m}^2/\text{gm}$, the highest nitride content obtained was only 0.18%.

These unsuccessful attempts to prepare tungsten nitride were not surprising in view of several literature references^(6, 21) which report that nitriding tungsten by nitrogen begins only at 2300°C . Stokes and Knipe⁽²²⁾ reported that tungsten nitride could not be prepared in a high-temperature plasma jet. The ease of formation of various nitrides was related to the temperature at which the free energy of formation equalled zero. Thus, titanium and magnesium nitrides were easily prepared with the plasma jet, but molybdenum and tungsten nitrides were not. It has been reported⁽²¹⁾ that the reaction of ammonia on finely divided tungsten at low temperatures ($250 - 360^\circ \text{C}$) formed tungsten imide as an intermediate compound.

Allen, Maykuth, and Jaffee⁽²³⁾ reported a maximum nitrogen pickup of only 20 ppm whether polycrystalline tungsten was treated in ammonia at 1000 to 1500°C for 11 hours, or treated in nitrogen at 2300°C for 6 to 12 hours.

It is interesting to note that the results reported in Table 16 (tungsten powder), when rearranged in order of increasing temperature, indicate that an appreciable decrease in the surface area of tungsten powder occurs at about 800°C or higher, regardless of hold time or whether an ammonia or nitrogen atmosphere was used. These data correlate rather closely with those shown in Figure 33 which is discussed in a subsequent section.

Sintered Compact Studies - Isostatically pressed compacts were made from the various batches of tungsten powder obtained from the nitriding experiments and sintered for 3.0 hours at 1500°C in hydrogen to determine the effect of nitrogen on the sinterability. The results are given in Table 17. The compacts sintered from tungsten powder Batches N-4, N-6, and N-8 containing relatively high nitrogen (600 to 1800 ppm N), gave densities that were 95-96% of theoretical, indicating that nitrogen does not interfere with sinterability.

The relatively low sintered densities (approximately 91% of theoretical) shown by the other batches of nitrided powder are in general agreement with the expectations based on surface area and preparation history. The low nitride contents ($< 100 \text{ ppm N}$) of four of the sintered compacts shown in Table 17 indicate that nitrogen is liberated during sintering.

Table 17
EFFECT OF NITROGEN ON THE SINTERED DENSITY

Batch Number	Tungsten Powder			Sintered Density		Nitrogen Content of Sintered Compact (ppm)
	Nitrogen (ppm)	Oxygen (%)	Surface Area (m ² /gm)	(gms/cc)	(avg % TD)	
N-11	2713	0.80	4.89	16.61 17.07 17.59	89.8	-
N-4	1790	1.66	10.54	18.39 18.48 18.43	95.5	100
N-9	1474	1.50	4.08	17.50 17.61 16.89	89.8	-
N-8	672	1.68	8.82	18.30 18.42	95.1	26
N-6	604	1.71	7.67	18.45 18.54 18.40	95.7	28
N-10	257	1.42	4.83	17.43 17.52	90.1	-
N-3	242	0.09	0.95	15.87	82.2	-
N-12	215	1.69	4.52	17.91 17.41 17.21	90.7	-
N-1	174	-	4.00	17.35 17.05 16.94	88.7	-
N-2	131	1.18	-	17.46 16.79 17.44	89.3	-
N-5	108	0.45	0.09	-	-	-
X	184	1.10	5.63	17.57 17.00	89.5	50

A comparison of the nitride content of several typical batches of laboratory-prepared tungsten powders and sintered pellets prepared from these powders is given in Table 18. The pellets were sintered in flowing hydrogen at 1500° C for three hours. These data show that the nitride content was reduced to below 60 ppm N by this sintering treatment.

Sintered Loose Powder Studies - The effect of the sinter temperature on the nitride content of tungsten powder was studied by heating approximately 100 grams of loose tungsten powder contained in Alundum boats in flowing hydrogen at various temperatures, using a hold time of 3.0 hours. Results, shown in Figure 32, show that much of the nitrogen is readily liberated from tungsten at elevated temperatures. Thus, large quantities of nitrogen would not be expected to be retained or precipitated at grain boundaries of sintered tungsten compacts. Whether the small remaining amount of nitrogen can produce a major influence on mechanical properties is still unknown.

Table 18
REDUCTION OF THE NITRIDE CONTENT BY SINTERING

Unsintered Tungsten Powder		Sintered Tungsten Compact ⁽¹⁾	
Batch Number	Nitrogen (ppm)	Compact Number	Nitrogen (ppm)
W-32	464	S 32 B	31
W-37	462	S 37 A	14
W-39 T	303	S 39 TB	< 10
W-41 T	150	S 41 TA	28
W-40 T	155	S 40 TA	50
W-31	145	S 31 I	15
W-27	377	S 27 I	23
W-15	416	S 15 D	12
W-16 D	474	S 16	58
Company B, Type II	213	SR-10	55

(1) Pressed isostatically at 30,000 psi and sintered for 3.0 hours at 1500° C in flowing H₂.

Figure 32. EFFECT OF TEMPERATURE ON THE NITRIDE CONTENT OF TUNGSTEN POWDER. (Soak Time - 3.0 Hours)

In conjunction with this study, the surface areas of the loosely sintered tungsten powders were obtained. Results, given in Figure 33, show a rapid decrease in the surface area at temperatures in excess of 700° C in a flowing hydrogen atmosphere. Although general agreement of the surface area values

Figure 33. EFFECT OF THE SINTERING TEMPERATURE ON THE SURFACE AREA OF TUNGSTEN POWDER. (Soak Time - 3.0 Hours)

are shown between the BET and Sorptometer methods, the latter method was still in the development stage of investigation.

Effect of Additives - To determine the effect of silicon and nitrate on the sinterability of laboratory-prepared tungsten powders, three batches of tungstic oxide were spiked with silicic acid and one batch was spiked with ammonium nitrate. The tungstic oxides used were prepared by wet-chemical precipitation methods and represented relatively high and low surface areas. Results, as shown in Table 19(A), indicate that neither silicic acid nor ammonium nitrate additives up to 0.1% and 0.2%, respectively, interfere significantly with the sintered density. Although sintered densities obtained from Runs A-35 (0.5% Si) and A-49 (0.2% Si) were less than 91% of the theoretical density, these low densities probably resulted from the relatively high oxide contents associated with these powders.

Spectrographic analyses of the sintered compacts made from these powders are shown in Table 20. These data show that silica was retained during the hydrogen reduction treatment of the tungstic oxide and after sintering in hydrogen at 1500° C, but that ammonium nitrate was decomposed to a residual nitrogen content of 43 ppm N.

The results in Table 19(A) also indicate that silicon may interfere with particle growth during reduction as evidenced by the increase in the surface area obtained by reducing tungstic oxide having either a relatively high or low surface area in the presence of silica. Reduction of the high-surface-area tungstic oxide in the absence

Table 19
EFFECT OF SILICON AND NITRATE ADDITIVES ON REDUCTION AND SINTERABILITY

Run Number	Tungstic Oxide Surface Area (m ² /gm)	Additive	Reduction Conditions ⁽¹⁾		Tungsten Powder					Sintered Pellet Density ⁽²⁾										
			H ₂ Flow (l/min)	Temperature (° C)	Surface Area (m ² /gm)	Percent O ₂	Crystallite Size (Å)			(gms/cc)	(% TD)									
							High	Low	Avg											
(A) A-11	30.4	None	12.0	700	2.67	0.41	1100	1025	1063	18.22	94.4									
										18.18	94.2									
										18.33	95.0									
A-40	30.4	0.2% NH ₄ NO ₃	12.0	700	2.06	0.68	1015	980	998	18.50	95.9									
										18.35	95.1									
A-34	30.4	0.1% H ₂ SiO ₃	12.0	700	3.81	0.61	915	890	903	18.25	94.6									
										18.14	94.0									
A-35	30.4	0.5% H ₂ SiO ₃	12.0	700	8.30	1.36	915	890	903	16.28	84.4 ⁽³⁾									
										15.78	81.8									
A-43	7.9	None	12.0	700	4.9	1.03	555	524	540	18.16	94.1									
										18.19	94.2									
										18.24	94.5									
										18.21	94.4									
A-10	7.9	None	12.0	700	5.8	0.83	533	524	529	18.34	95.0									
										18.44	95.5									
										18.32	94.9									
										18.49	95.8									
A-49	7.9	0.2% H ₂ SiO ₃	12.0	700	8.5	1.56	519	499	509	17.41	90.2									
										17.55	90.9 ⁽²⁾									
(B) SI-1	24.4	None	12.0	700	4.96	0.64	582	523	553											
										SI-2	0.5% H ₂ SiO ₃	12.0	700	8.81	1.18	454	442	448		
										SI-3	0.5% SiO ₂ (Ottawa sand)	12.0	700	6.63	0.65	523	453	488		
										SI-4	None	5.0	700	7.54	0.90	418	402	410		
										SI-5	0.5% H ₂ SiO ₃	5.0	700	12.82	1.76	418	384	401		
										SI-6	0.2% Cab-O-Sil	5.0	700	10.45	0.95	386	378	382		
										(C) SI-7A(4)	24.4	None	1.0	750	5.17	0.49	683	608	646	
SI-7B(5)					0.95	8.11														
SI-8A(6)	24.4	0.2% Cab-O-Sil	1.0	750	5.59	0.62	495	450	473											
SI-8B(5)					2.09	7.38														

(1) 4.0 hours.

(2) Pressed isostatically at 30,000 psi and sintered for 3.0 hours in flowing H₂ at 1500° C.

(3) High oxide content of this powder probably caused relatively low density.

(4) Incomplete reduction; gray-black product estimated at 72% of theoretical conversion.

(5) Unconverted brown WO₂ portion of product.

(6) Incomplete reduction; gray-black product estimated at 58% of theoretical conversion.

Table 20
SPECTROGRAPHIC ANALYSIS OF SINTERED TUNGSTEN PELLETS
AS PREPARED FROM TUNGSTIC OXIDE SPIKED WITH
AMMONIUM NITRATE AND SILICIC ACID
(All Values in Parts Per Million)

	Pellet Numbers		
	A 40-1(1)	A 49-1(2)	A-35-1(3)
Ag	< 1	< 1	< 1
Al	60	60	10
Bi	< 30	< 30	< 30
Ca	10	3	< 3
Co	< 30	< 30	< 30
Cr	< 10	< 10	< 10
Cs	< 300	< 300	< 300
Cu	6	1	5
Fe	50	50	40
Mg	10	2	1
Mn	< 3	< 3	< 3
Mo	100	< 30	< 30
N	43	36	36
Na	< 30	< 30	< 30
Ni	100	10	10
Pb	< 30	< 30	< 30
Rb	< 300	< 300	< 300
Sb	< 30	< 30	< 30
Si	50	1500	3000
Sn	< 30	< 30	< 30
V	< 30	< 30	< 30
Th	< 100	< 100	< 100
Zr	< 30	< 30	< 30

(1) WO_3 doped with 0.2% NH_4NO_3 .

(2) WO_3 doped with 0.2% H_2SiO_3 .

(3) WO_3 doped with 0.5% H_2SiO_3 .

of silica gave tungsten powder having a surface area of $2.7 \text{ m}^2/\text{gm}$ (Run A-11); but with 0.5% Si present, tungsten powder having a surface area of $8.3 \text{ m}^2/\text{gm}$ (Run A-35) was obtained. Similarly, reduction of low-surface-area tungstic oxide gave tungsten powder having a surface area of $5 \text{ m}^2/\text{gm}$ (Run A-43) in the absence of silicon, but this was increased to $8.5 \text{ m}^2/\text{gm}$ (Run A-49) by the presence of 0.2% Si.

These results were somewhat surprising since Millner⁽¹⁷⁾ found that additions of K-Si-Al compounds in combination with tungstic oxide resulted in grain coarsening during reduction. Also, Spier and Wanmaker⁽²⁴⁾ reported that the addition of potassium silicate or potassium silicotungstate resulted in a marked growth of the tungsten particles during reduction. Additional studies on the effect of silica as an inhibitor to particle size growth during reduction were therefore made.

Reduction of 50-gram batches of updoped and doped tungsten oxide with various forms and particle sizes of silica, silicic acid, SiO_2 as -400 mesh Ottawa sand, and Cab-O-Sil, at 700°C using hydrogen flowrates of 5 and 12 liters per minute showed that silica produced an apparent increase in the surface area of the tungsten metal powder under equivalent conditions. Results are shown in Table 19(B). Since the

oxide content of those tungsten powders containing silica are higher than the corresponding powders obtained in the absence of silica, this increase in surface area may only be superficial when one considers the difference in particle density between tungsten metal (19.3 gms/cc) and tungsten dioxide (14.85 gms/cc). The higher oxide content of these silica-doped powders may be due to their incomplete conversion to tungsten metal, and the tungsten metal powder product obtained from the silica-doped runs may have actually consisted of an admixture of tungsten metal and tungsten dioxide.

Two runs comparing the reduction of silica-free tungstic oxide and oxide doped with 0.2% Cab-O-Sil under equivalent conditions using an extremely low hydrogen flow rate at 750° C indicated that silica slows the rate of the reduction reaction. Results are shown in Table 19(C). Both runs showed the presence of some unconverted, brown dioxide at the outlet gas end of the reduction boat, but a much larger quantity of unreacted dioxide resulted from the silica-doped oxide. The unconverted, brown tungsten dioxide and converted tungsten metal powder products from both runs were sampled separately. The brown portions from the reduction of the undoped oxide (SI-7B) and silica-doped oxide (SI-8B) were approximately 9.5 and 16 grams, respectively. As shown in Table 19(C), the essentially equivalent oxygen contents of the gray-metal products (SI-7A and 8A) and tungsten dioxide portions (SI-7B and 8B) resulting from these runs indicate that an equitable division of the product from both runs had been made. Particle size distribution analyses of the silicic acid powder and -400 mesh Ottawa sand used for the tungstic oxide doping experiments are plotted in Figure 34. The Cab-O-Sil silica^(e) used had a particle size range of 0.015 to 0.020 micron.

Two hydrogen reduction runs on 5-gram samples of high-surface-area tungstic oxide (24.4 m²/gm) were made using platinum boats (3" x 1/2" x 1/4") to further show the retardation of the rate of WO₃→W reaction by silica. Both runs were made under equivalent reduction conditions; ie, a hydrogen flow rate of 1 liter/minute, a 35-minute heating cycle, and a 10-minute soak period at 850° C. Flowing hydrogen was used throughout the cooling cycles. One of these runs employed undoped tungstic oxide and the other run consisted of the same batch of tungstic oxide which had been doped with 0.2% Cab-O-Sil by tumbling.

The product resulting from the hydrogen reduction of the undoped trioxide was black, had a net weight of 2.6 grams, and an average crystallite size of 372 Å. The product resulting from the doped trioxide was brown (presumably WO₂) at the bottom and at the top surface of the platinum boat (at the outlet gas end), indicating incomplete conversion to metal. The net weight of the product was 3.7 grams and had an average crystallite size of 330 Å. This product also appeared to be much coarser than the undoped product when viewed with the naked eye. Surface area and oxygen

(e) Manufactured by G. F. Cabot, Inc.

Figure 34. PARTICLE SIZE DISTRIBUTION ANALYSES OF THE SILICA USED IN DOPED TUNGSTIC OXIDE REDUCTION STUDIES.

content of the product from the reduction of the undoped and doped oxides were $4.33 \text{ m}^2/\text{gm}$ and $6.8\% \text{ O}_2$, and $4.75 \text{ m}^2/\text{gm}$ and $8.2\% \text{ O}_2$, respectively. Thus, under equivalent reduction conditions, small additions of silica to tungsten trioxide will retard the rate of the reduction reaction considerably.

It could not be established by X-ray diffraction whether or not silica used in the oxide doping experiments entered the tungsten metal lattice during reduction since the diffraction patterns appeared to be the same as the tungsten standard, and impurity percentages less than 5% usually cannot be detected. According to Millner,⁽¹⁷⁾ "the tungsten atoms in the crystal lattice of metallic tungsten may be regarded as packed spheres $2.8 \text{ \AA}$ in diameter. Since the diameter of silicon atoms are $1.15 \text{ \AA}$, it would be possible for the silicon to occupy positions in the tungsten lattice by substitution or interstition".

It was also observed that tungsten powder having a surface area $> 5 \text{ m}^2/\text{gm}$ as made by the reduction of silica-doped tungstic oxide appeared to have a lesser tendency toward pyrophoricity; however, further work is needed to establish the quantitative aspects of any stabilization effect by silica.

Effect of Oil Contamination - The effect of oil contamination on the sintered density of tungsten compacts was studied using two tungsten powder compacts that had been deliberately soaked with mineral oil. These compacts were pressed isostatically at

30,000 psi using punctured latex finger cots loaded with commercial tungsten powder (Company C). The compacts were sintered simultaneously with four other commercial (Company C) powder compacts (pressed isostatically at 30,000 psi) for 3.0 hours at 1500° C in flowing hydrogen.

After removing the two oil-soaked compacts from the sintering furnace it was observed that approximately ten cubic centimeters of mineral oil had condensed at the cool, outlet end of the Morganite sintering tube, indicating that most of the oil had been distilled from the pellets. The sintered densities of these pellets were 13.8 and 14.5 gms/cc, respectively, or approximately 71 - 75% of the theoretical density. The average sintered density of the four Company C compacts that had not been oil contaminated was 16.8 gms/cc, or about 87% of the theoretical density.

Examination of the two oil-soaked pellets after sintering showed that both contained cracks, probably resulting from the volatilization of oil during the sintering treatment. No cracks were observed for the four compacts that had not been oil soaked. The carbon content of one of the oil-soaked compacts after sintering was 2338 ppm compared to only 107 ppm carbon for one of the compacts that was not oil soaked.

Shrinkage and Densification - In a previous discussion (Page 45) of the relationship between the surface area of tungsten powder and the green (pressed) density, it was stated that compacts pressed isostatically at 30,000 psi from laboratory-prepared tungsten powders exhibit a lower green density than compacts pressed from coarser, commercial tungsten powders. After sintering these compacts for 3.0 hours at 1500° C in flowing hydrogen, the laboratory-prepared compacts undergo extensive shrinkage and attain considerably higher densities than compacts prepared from commercial powders. A comparison of the green and sintered densities for laboratory-prepared and various commercial powders is shown in Figure 35. The comparative shrinkage of sintered tungsten pellets and tungsten rods (sintered in flowing hydrogen for 3.0 hours at 1500° C) made from various commercial and laboratory-prepared tungsten powders is shown in Figures 36 and 37, respectively.

A study was made of the effect of temperature on the degree of linear shrinkage obtained for tungsten rods pressed isostatically at 30,000 psi and sintered in flowing hydrogen for 3.0 hours at various temperatures. A medium-grade laboratory-prepared tungsten powder (surface area - 4.9 m²/gm; O₂ - 1.1%) and two typical commercial tungsten powders were compared. The extent of linear shrinkage was obtained by a measurement of the fiducial points on the surface of the compact, before and after sintering. The percentage of shrinkage (s) was calculated from the relationship:

$$S = \frac{\text{Change in Length}}{\text{Unsintered Length}} \times 100.$$

Results, as given in Figure 38, indicate that linear shrinkage of the compacts made from laboratory-prepared powders starts at approximately 750° C, and that a temperature greater than 1100° C is required before a shrinkage of the compacts made

Figure 35. COMPARISON OF GREEN AND SINTERED DENSITIES FOR LABORATORY-PREPARED AND COMMERCIAL TUNGSTEN POWDERS.

from commercial tungsten powder occurs. Similar differences in the sintering behavior of various tungsten metal powders having different particle sizes and derived from different manufacturing processes were reported by Dawihl. (25)

It is significant to note that the temperature at which linear shrinkage begins for the laboratory-prepared tungsten (ie, 750° C) is in close agreement with the temperature at which a significant decrease in the surface area of laboratory-prepared tungsten powder occurs, as shown in Figure 33. A foreknowledge of the degree of shrinkage for various tungsten powders upon sintering is especially important in the fabrication of larger, production-sized, sintered tungsten bodies (ie, rocket nozzles) by isostatic pressing where close tolerance of the sintered body must be met to minimize difficult and costly machining operations.

An associated study of the extent of densification obtained for various tungsten compacts pressed isostatically at 30,000 psi and sintered for 3.0 hours in flowing hydrogen at various temperatures has also shown that laboratory-prepared tungsten powders begin to sinter at appreciably lower temperatures than the commercial powders. Results are shown in Figure 39.

Improving the Sinterability by Post-Reduction Treatment

An attempt was made to improve the sinterability of three batches of laboratory-prepared tungsten powder containing 1.1, 2.2, and 3.4% oxygen by post-reduction

105766(U)

Figure 36. COMPARATIVE SHRINKAGE OF COMMERCIAL AND LABORATORY-PREPARED TUNGSTEN PELLETS. (Pressed Isostatically at 30,000 PSI and Sintered for 3.0 Hours at 1500°C in Flowing Hydrogen)

treatment of these powders in flowing hydrogen at 700° C to lower the oxygen content. Results, as summarized in Table 21, showed that the greatest improvement in the sintered density was shown by the tungsten powder containing the highest oxygen content. Compacts pressed isostatically from this powder at 30,000 psi sintered to only approximately 80% of the theoretical density. Upon a second reduction of this powder with hydrogen at 700° C, the oxygen content was lowered to 0.8% and compacts pressed isostatically at 30,000 psi sintered to 95 - 96% of the theoretical density.

Chemical Purity

A comparison of the chemical purity of typical commercial and laboratory-reduced tungsten powders prepared by wet-chemical precipitation of tungstic oxide is shown in Table 22. Also shown are partial spectrographic analyses of commercial APT, laboratory-purified APT, and tungstic oxide and tungsten metal powder derived from commercial tungsten. The metallic impurity levels shown for the laboratory-prepared powders were, in most cases, at or below their detectable limits of accuracy for the spectrographic method of analysis used. The commercial tungsten powders appear to

105765(U)

Figure 37. COMPARATIVE SHRINKAGE OF COMMERCIAL AND LABORATORY-PREPARED TUNGSTEN RODS. (Pressed Isostatically at 30,000 PSI and Sintered for 3.0 Hours at 1500°C in Flowing Hydrogen)

have essentially equivalent purity, except for slightly higher iron, nickel, and molybdenum contents in some cases.

The chemical purity of several typical sintered tungsten compacts made from commercial tungsten powder, oxidized commercial tungsten powder, wet-chemical tungstic oxide, and tungsten powder derived from APT is shown in Table 23. Although these results show relatively small differences in the impurity content between the various types of tungsten powders, a difference in the sintered density from 72% to 93% of the theoretical density is represented. Thus, other factors in addition to the chemical purity with respect to metallic impurities have a greater effect on the powder sinterability (eg, oxide content).

Figure 38. LINEAR SHRINKAGE OF VARIOUS TUNGSTEN POWDER COMPACTS AS A FUNCTION OF THE SINTERING TEMPERATURE. (Sintered for 3.0 Hours in Hydrogen)

Since a change in the spectrographic limits was made during the course of this investigation, some variation in the elements that were scanned and their detection limits are shown in Tables 22 and 23.

Improving the Sinterability of the Commercial Powders

A study was made to improve the sinterability of commercial tungsten powder by oxidation to tungstic oxide in a muffle furnace maintained at 500° C and reducing with hydrogen at 650 - 700° C. Results are shown in Table 24. Although the surface area of the tungsten powders produced was high (approximately 10 m²/gm), the oxygen content was correspondingly high (1.5 - 3.1%) and sintered densities of only 85 - 90% of theoretical were obtained. The high oxide contents of the tungsten powders reduced at 650° C may be attributed to the presence of unusually large amounts of β -tungsten, which is really an oxide. Charlton(26) states that the first stage in the reduction of tungstic oxide is always the β -oxide and an insufficient reduction time at the lower temperature may have been responsible for the incomplete conversion to metal.

It is possible that under more favorable conditions of preparation and/or powder handling, a more sinterable powder could be produced from commercial metal powder.

Figure 39. DENSIFICATION OF ISOSTATICALLY PRESSED COMPACTS MADE FROM COMMERCIAL AND LABORATORY-PREPARED POWDERS AFTER SINTERING AT VARIOUS TEMPERATURES.

Table 21
IMPROVEMENT OF SINTERABILITY BY HYDROGEN TREATMENT

Pellet Number(1)	Untreated Tungsten Powder				H ₂ -Treated Tungsten Powder(3)			
	Surface Area (m ² /gm)	Percent O ₂	Sintered Density(2) (gms/cc)	(% TD)	Surface Area (m ² /gm)	Percent O ₂	Sintered Density (gms/cc)	(% TD)
X-1	5.63	1.10	17.01	88.1	-	-	17.75	92.0
X-2	5.63	1.10	17.07	88.4	-	-	17.84	92.4
X-3	5.63	1.10	16.81	87.1	-	-	-	-
Y-8	5.49	2.27	16.83	87.2	-	0.57	17.94	93.0
Y-15	5.49	2.27	16.64	86.2	-	-	17.98	93.2
Y-22	5.49	2.27	16.75	86.8	5.02	0.59	17.57	91.0
Z-1	6.51	3.36	15.45	80.1	-	0.78	18.53	96.0
Z-2	6.51	3.36	15.78	81.8	-	-	18.43	95.5
Z-3	6.51	3.36	15.33	79.4	-	-	-	-

(1) Pressed isostatically at 30,000 psi.

(2) Sintered 3.0 hours at 1600° C in flowing hydrogen.

(3) Powder was reduced a second time in flowing hydrogen for four hours at 700° C.

Sintered compact densities that are 95% of the theoretical density have been realized from two pellets pressed at 30,000 psi from a single batch that was derived from oxidized Company B, Type II commercial powder (see Figure 29), but these results have not been reproducible because of the difficulty in controlling the oxygen content of high-surface-area powders to less than one percent.

Table 22
CHEMICAL PURITY OF COMMERCIAL AND LABORATORY-PREPARED TUNGSTEN POWDERS
(All Values in PPM)

Impurity	Commercially Derived Powders					Laboratory-Prepared Powders		
	Company B		Company A	Oxidized from Company B, Type I Tungstic Oxide	Oxidized from Company B, Type II Tungstic Oxide	APT(1)	Tungstic Oxide(1)	Tungsten(2)
	Type II	Type I						
Ag	< 1	< 10	6	< 10	10	< 10	< 10	< 10
Al	15	< 40	< 30	< 40	< 40	< 40	< 40	< 40
Ca	< 3	< 100	30	< 100	< 100	< 100	< 100	< 100
Co	< 30		< 30					
Cr	< 15		< 100					
Cu	4	< 10	6	< 10	15	< 10	< 10	< 10
Fe	60	100	150	100	100	< 100	< 100	< 100
Mg	30	< 100	30	< 40	< 100	< 100	< 100	< 100
Mn	20	40	< 10	< 40	40	< 40	< 40	< 40
Mo	< 30	400	< 30		< 40	< 40	< 40	< 40
Na	30	-	100					
Ni	20	80	< 30	60	< 40	< 40	< 40	< 40
Pb	< 30	-	< 30					
Si	10	< 100	30	< 100	< 100	< 100	< 100	< 100
Sn	< 30	-	< 30					
V	< 30	< 40	-	< 40	< 40	< 40	< 40	< 40
Zr	< 30	< 40	< 30	< 40	< 40	< 40	< 40	< 40

(1) Prepared by wet-chemical precipitation.

(2) Prepared by hydrogen reduction of tungstic oxide from wet-chemical precipitation.

Microstructure

Photomicrography - The microstructure of sintered compacts of commercial and laboratory-prepared tungsten powders has been studied in an attempt to evaluate the sintered density with other quality characteristics of the powder. Photomicrographs of several sintered tungsten metal compacts and a summary of the oxide and metal powder quality characteristics are shown in Figures 40 and 41. These compacts were sintered for 3.0 hours at 1500° C in flowing hydrogen.

The contrast between the large-sized grain structure shown by the high-density compacts having greater than 95% of the theoretical density (Pellets A9-4, 18A, A6-5, and P52A-2) compared to the smaller-sized grain structures with holes and voids for the less-dense compacts (Pellets R-5, 42BC, A26-4, and A9-1) is striking. Large differences in grain size and density are also shown for Pellet A9-1 (81% of TD) and Pellet A9-4 (95% of TD) made from the same batch of tungsten powder, but pressed isostatically at 10,000 psi and 38,000 psi, respectively.

For these microstructure studies the sintered compact was sectioned with a Buehler 1010 abrasive cut-off machine and mounted in a thermosetting phenolic molding material using an AB speed press. A two-step grinding procedure was then used, namely: (1) coarse grinding on 180-grit silicon carbide belts to establish a flat surface, and (2) fine grinding on wet silicon carbide metallographic papers (240, 320, 400, 600 and 4/0 grit) to establish a smooth surface. The specimen was then wet

Table 23
CHEMICAL PURITY OF SINTERED TUNGSTEN COMPACTS
(3.0 Hours at 1500° C in H₂)

Pellet Number	Percent of Theoretical Density	Origin	Reduction Temperature (° C)	Element (ppm)											
				Ag	Al	Ca	Cu	Fe	Mg	Mn	Mo	Ni	Si	V	Zr
S-30 I	72.9	APT	850	< 10	< 40	< 100	< 10	< 100	< 100	< 40	< 40	< 40	< 100	< 40	< 40
S-15 D	90.0	APT	750	< 10	< 40	< 100	60	100	< 100	< 40	< 40	50	< 100	< 40	< 40
27 I	87.3	WO ₃ from APT	750	< 10	< 40	< 100	10	100	< 100	< 40	< 40	80	< 100	< 40	< 40
S-R 10	83.9	Commercial(1)	-	< 10	< 40	< 100	< 10	100	< 100	< 40	< 40	40	< 100	< 40	< 40
A 15-1	75.3	WO ₃ from Commercial(2)	700	< 10	< 40	< 100	100	150	< 100	< 40	< 40	60	100	< 40	< 40
A 24-1	82.2	Lab-Prepcrd WO ₃	700	< 10	< 40	< 100	100	100	< 100	< 40	< 40	< 40	< 100	< 40	< 40
A 3-3	97.6	Lab-Prepcrd WO ₃	700	< 1	50	< 3	1	30	1	< 3	< 30	30	30	< 30	< 30
A 10-2	95.5	Lab-Prepcrd WO ₃	700	< 1	300	3	60	40	10	3	< 30	30	150	< 30	30

(1) Company B, Type II powder.

(2) Company B, Type I powder oxidized at 500° C.

Table 24
PREPARATION AND SINTERING OF TUNGSTEN FROM OXIDIZED COMMERCIAL POWDER
(H₂ Flow Rate During WO₃ Reduction = 12 Liters/Minute)

Batch Number	Tungstic Oxide Surface Area (m ² /gm)	Reduction Temperature (° C)	Reduced Tungsten Powder			Sintered Density(1)	
			Surface Area (m ² /gm)	Percent O ₂	Average Crystallite Size (Å)	(gms/cc)	(% TD)
A9	2.48(2)	700	4.69	1.90(3)	342	18.64	96.6
						18.42	95.4
						18.05	93.5
B1	2.48(2)	700	8.91	1.36	-	18.18	94.2
						18.16	94.1
						18.06	93.6
B2	2.48(2)	750	7.84	0.83	-	17.60	91.1
						17.55	90.9
						17.42	90.3
A12	2.23(4)	700	8.89	1.45	271	16.60	86.0
						16.61	86.0
						16.78	86.9
A23	2.23(4)	700	9.55	1.98	239	15.83	82.0
						15.72	81.5
						15.87	82.2
A28	2.23(4)	650	7.89	3.16	156	16.07	83.3
						16.62	86.1
						15.88	82.3
A29	2.23(4)	650	8.71	2.35	199	17.32	89.7
A30	2.23(4)	650	9.10	2.74	211	17.07	88.4
A36	2.48(2)	700	6.99	1.52	292	17.59	91.1
						17.72	91.8
						16.25	84.2
A42	1.42(4)	700	7.94	1.77	246	16.20	83.9
						15.88	82.3
						16.51	85.5
A48	1.42(4)	650	8.69	2.67	146	16.39	84.9
						16.42	85.1
						16.44	85.2
A55	1.42(4)	700	8.08	1.56	208	16.36	84.8
						17.09	88.5
						17.13	88.8
A57	1.42(4)	650	10.76	2.20	185	17.13	88.8
						16.44	85.2
						16.36	84.8
A58	1.42(4)	650	9.83	2.06	164	16.42	85.1
						16.36	84.8
						16.42	85.1

(1) 3.0 hours at 1500° C in hydrogen.

(2) From Company B, Type II; Surface Area 0.7 m²/gm.

(3) Suspect oxygen content was actually much lower than shown.

(4) From Company B, Type I; Surface Area 0.14 m²/gm.

polished with diamond paste (1 μ) on a high-speed (1750 rpm) polishing wheel covered with Buehler Duracloth followed by a low-speed (163 rpm) polish with Gamal cloth. Finally, the specimen was electroetched with 10% sodium hydroxide to outline the grain boundaries.

Pellet A9-1

1000X

Pellet A9-4

1000X

81.2
10,000
Oxidized Company B, Type II
3.5
700

Sintered Density (% TD)
Compacting Pressure (psi)
WO₃ Origin
WO₃ Surface Area (m²/gm)
Reduction Temperature (°C)

95.4
38,000
Oxidized Company B, Type II
3.5
700

4.69
1.90
342

Reduced Tungsten Powder
Surface Area (m²/gm)
Oxygen Content (%)
Average Crystallite Size (Å)

4.69
1.90
342

Pellet R-5

1000X

Pellet 42BC

1000X

78.0
30,000
Company B, Type II
Company B, Type II
Company B, Type II

Sintered Density (% TD)
Compacting Pressure (psi)
WO₃ Origin
WO₃ Surface Area
Reduction Temperature (°C)

66.2
30,000
Wet Chemical Precipitation
20.4
850

0.7
0.27
1,018

Reduced Tungsten Powder
Surface Area (m²/gm)
Oxygen Content (%)
Average Crystallite Size (Å)

2.58
0.23
593

Figure 40. PHOTOMICROGRAPHS OF SINTERED TUNGSTEN PELLETS. (Pellets A9-1, A9-4, R-5, and 42BC)

Pellet A26-4

1000X

Pellet A6-5

1000X

89.7
30,000
Wet Chemical Precipitation
10.85
700

Sintered Density (% TD)
Compacting Pressure (psi)
WO₃ Origin
WO₃ Surface Area (m²/gm)
Reduction Temperature (°C)

98.1
30,000
Wet Chemical Precipitation
52.8
700

9.88
3.18
185

Reduced Tungsten Powder
Surface Area (m²/gm)
Oxygen Content (%)
Average Crystallite Size (Å)

5.22
1.02
519

Pellet 18A

1000X

Pellet P52A-2

1000X

96.9
30,000
Wet Chemical Precipitation
17.49
750

Sintered Density (% TD)
Compacting Pressure (psi)
WO₃ Origin
WO₃ Surface Area (m²/gm)
Reduction Temperature (°C)

94.2
30,000
Wet Chemical Precipitation
13.4
700

5.83
1.07
368

Reduced Tungsten Powder
Surface Area (m²/gm)
Oxygen Content (%)
Average Crystallite Size (Å)

12.63
1.63
242

Figure 41. PHOTOMICROGRAPHS OF SINTERED TUNGSTEN PELLETS. (Pellets A26-4, A6-5, 18A, and P52A-2)

Fractography and Electron Microscopy - Fourteen sintered tungsten compacts were examined with an electron microscope in an attempt to obtain information relating to the oxide impurity of the compact. Two types of specimens were prepared from each sample: a fracture surface and a polished-and-etched section. It was hoped that the fracture surface analyses (fractographs) might have revealed the fraction of the grain surface area that was covered with oxide so that the oxide content of the sintered compact could be related to the sintered density. Such fractographs^(27,28) have been most useful in relating the impurity content of coarse-grained metals such as arc-cast molybdenum ingots with mechanical and other properties.

The major conclusion reached from the examination of the fracture surfaces was that sintered compacts made from Company B, Type II-grade powder had sufficient porosity so that the mode of fracture (trans or intergranular) could not be determined. Fractographs of sintered compacts made from tungsten powders prepared in this laboratory by hydrogen reduction showed definite intergranular fractures. "The bumps scattered about the fracture surface could be impurity sites, very fine crystals, porosity or bubbles, and replication artifacts. In general, the size of the crystallite agrees with the appearance of the polished and etched microstructures."⁽²⁹⁾ Typical electron micrographs of polished-and-etched surfaces and on fractured tungsten compacts are shown in Figures 42 and 43, respectively. Since the fracture surfaces were too rough for optical examination, replicas were prepared by making an impression of the surface on cellulose acetate. The plastic was shadowed with palladium, coated with carbon, then dissolved away, leaving the carbon replica which was mounted on a 200-mesh grid for electron microscope examination.

Company B, Type II Tungsten Powder
Pellet No R-8

Sintered Density	76.4% of TD
Tungsten Powder	
Surface Area	0.7 m ² /gm
Oxygen Content	0.3%

Laboratory-Prepared Tungsten Powder
Pellet No L-16-1

Sintered Density	94.9% of TD
Tungsten Powder	
Surface Area	10.12 m ² /gm
Oxygen Content	1.70%

Figure 42. ELECTRON PHOTOMICROGRAPHS OF POLISHED-AND-ETCHED SURFACES OF SINTERED TUNGSTEN PELLETS. (Sintered for 3.0 Hours at 1500°C in Flowing Hydrogen; 8800X)

The polished and etched microsections were prepared in the following manner:

1. Mounted in a room-temperature-setting epoxy resin.

Pellet R-2

Pellet R-8

Company B, Type II Tungsten Powder

Sintered Density	77.3% of TD
Tungsten Powder	
Surface Area	0.7 m ² /gm
Oxygen Content	0.3%

Sintered Density	76.4% of TD
Tungsten Powder	
Surface Area	0.7 m ² /gm
Oxygen Content	0.3%

Pellet A45-2

Pellet L-16-1

Laboratory-Prepared Tungsten Powder

Sintered Density	89.6% of TD
Tungsten Powder	
Surface Area	13.84 m ² /gm
Oxygen Content	3.70%

Sintered Density	94.9% of TD
Tungsten Powder	
Surface Area	10.12 m ² /gm
Oxygen Content	1.70%

Figure 43. ELECTRON PHOTOMICROGRAPHS OF FRACTURED SURFACES OF SINTERED TUNGSTEN PELLETS. (Sintered for 3.0 Hours at 1500°C in Flowing Hydrogen; 3600X)

2. Ground flat with a belt grinder.
3. Ground on hand papers through 600 grit.
4. Polished on a vibrating polisher with Linde A.
5. Polished on a vibrating polisher with Linde B.
6. Etched with a sodium hydroxide-potassium ferricyanide solution.

Replicas were then prepared from the etched specimens for electron microscope examination.

"Examination of the polished-and-etched specimens did not lead to any real difference which could be related to any process variable, except that the low-density samples (A-36-2, R-2, R-8, A48-X) were indeed porous. The etch used acted quite rapidly and attacked in a manner that was orientation dependent." (29)

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

DISCUSSION

As a general conclusion, reduction of tungstic oxide having a relatively low surface area under optimum conditions of a high hydrogen flow rate and a low temperature will give a tungsten powder that can be sintered to greater than 95% of the theoretical density. Conversely, reduction of tungstic oxide having a relatively high surface area under adverse conditions of a low hydrogen flow rate and a high temperature results in a tungsten powder that cannot be sintered to a high density. For example, an inspection of Table 11 shows that sintered densities of only 90% of theoretical were obtained from tungstic oxide that was prepared by an ion-exchange technique (Batch W-50; SA = $7.2 \text{ m}^2/\text{gm}$) and reduced at 750°C in a double boat (ie, arranged "piggy back") using a relatively low hydrogen flow rate of 4.4 liters per minute. Reduction of this material in a single boat at 700°C with an increased hydrogen flow rate of 9.8 liters per minute produced a marked improvement in the sintered density; ie, approximately 95 - 97% of theoretical.

The harmful effect of oxygen in tungsten metal powder is clearly shown by a study of the sintering results with powders prepared from Batch W-57 tungstic oxide having a surface area of $30 \text{ m}^2/\text{gm}$ at 12 liters H_2 per minute (Table 11). These oxygen contents (0.24 - 0.58%) were the lowest obtained in this series of tests, and the sintered densities for all six pellets were above 96% of theoretical. These results were obtained with tungsten powders having relatively low surface areas ($1.7 - 2.0 \text{ m}^2/\text{gm}$) and strongly suggest that some sacrifice of surface area is justified in order to decrease the oxygen content of the metal powders. This fact is also indicated by the results shown in Table 12 showing that only approximately 85% of the theoretical density was obtained after sintering pellets made from ultra-fine Company C commercial tungsten powder (SA = $14.9 \text{ m}^2/\text{gm}$) for 3.0 hours at 1500°C . The poor sinterability of this powder is probably due to the high oxide content (1.3% O_2) associated with the highly reactive particle surfaces.

Sintered pellet densities of approximately 90% of theoretical have been obtained from the reduction of commercial APT or the trioxide derived from commercial APT. It has not been possible to obtain sintered pellet densities greater than approximately 90% of theoretical even though recrystallized and purified APT was used as the intermediate compound for preparing the powder by hydrogen reduction and high-surface-area powders were obtained.

In general, sinterability of tungsten powder depends upon several interrelated variables: surface area, oxygen content, nitrogen content, chemical purity, reduction temperature, and isostatic forming pressure. Although a high oxygen content of tungsten powder has been shown to produce an adverse effect on sinterability, control of this variable has been extremely difficult. Upon preparing a batch of freshly reduced tungsten powder, certain powder-handling steps were necessary to obtain a sample of the powder for analytical purposes and to prepare compacts by isostatic

pressing. Since suitable equipment to allow complete handling of the freshly reduced powder from the time of preparation until final sintering of the pressed compact without exposure to air was not available for this study, no close control of the oxygen content of the various powder batches was realized.

ACKNOWLEDGEMENTS

The assistance of the following is gratefully acknowledged: R. L. Sherman, Oak Ridge National Laboratory for crystallite size determinations; T. E. Willmarth, Oak Ridge National Laboratory for electron photomicrographs of tungsten powders; and Warren Bridges, Oak Ridge National Laboratory for fractography studies.

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

REFERENCES

1. Levy, A. V.; Metal Progress, pp 81-82, March 1961.
2. Neeley, A. C.; Production of Tungsten Rocket Nozzle Inserts, Y-1343; Union Carbide Corporation-Nuclear Division, Y-12 Plant, Oak Ridge, Tennessee; December 12, 1960.
3. Anonymous; Hot-Pressed Tungsten for Rocket Nozzles, Final Report to Aerojet-General Corporation; Haynes-Stellite Company, Kokomo, Indiana; April 1961.
4. Saunders, N. T.; Experimental Method of Producing Porous Tungsten for Ion Rocket Engines, NASA-D864; June 1961.
5. Goodwin, H. B. and Greenridge, C. T.; Metal Progress, p 812; June 1957.
6. Materials Advisory Report of the Committee on Refractory Metals, II, p 195, MAB-154-M; National Academy of Sciences - National Research Council, Washington, D. C.; October 15, 1959.
7. Toensing, C. H.; "Review - The Fabrication of Tungsten", ASTM Special Technical Publication No. 272, Symposium on Newer Metals; American Society for Testing Materials, Philadelphia, Pennsylvania (1960).
8. Kopelman, B.; American Instrument Mining and Metal Engineers, Technical Publication No. 2100; October 1946.
9. Smithells, C. J.; Tungsten, p 51; Chemical Publishing Company (1953).
10. Li, K. C. and Wang, C. Y.; Tungsten, p 214; Reinhold Publishing Company (1955).
11. Jones, D. J.; J Less Common Metals, 2, pp 76-85 (1960).
12. Hampel, C. A.; Ind Eng Chem, 53, p 91 (1961).
13. Asbury, J. J.; Personal Communication.
14. Goetzel, C. G.; Treatise on Powder Metallurgy, 1, p 118; Interscience Publishers, Inc (1949).
15. Montgomery, C. D.; Personal Communication.
16. Lambdin, F.; Personal Communication.

17. Millner, T.; "Scientific Principles in the Production of Metallic Tungsten for the Electric Lamp Industry and the Control of Its Characteristics", Acta Technical Acad Sci Hung, 17, AEC-tr-3125, pp 67-112 (1957).
18. Millner, T. and Neugebauer, J.; Nature, 163, pp 601-602 (1949).
19. Gulbransen, E. A., Phelps, R. T., and Hickman, J. W.; Ind Eng Chem, Anal Ed, 18, p 640 (1946).
20. Mantell, C. L.; Industrial Carbon, p 418; D. Van Nostrand Co, Inc (1946).
21. Schwarzkopf, P. and Kieffer, R.; Refractory Hard Metals, pp 252-253; MacMillan Company (1953).
22. Stokes, C. S. and Knipe, W. W.; Ind Eng Chem, 52, p 288; April 1960.
23. Allen, B. C., Maykuth, D. J., and Jaffee, R. I.; The Effects of Impurities on the Properties of Tungsten, p 9; AFSWC-TR-60-6; Air Force Special Weapons Center; December 15, 1959.
24. Spier, H. L. and Wanmaker, W. L.; Phillips Research Reports, 13, pp 149-156 (1958).
25. Dawihl, W.; Sintering Experiments with Tungsten Metal Powder, FD 3881/47; Hard Metal Research Association, Berlin.
26. Charlton, M. G.; Nature, pp 109-110 (1952).
27. Mallett, M. W.; The Determination of Oxygen, Nitrogen, Hydrogen, and Carbon in Molybdenum, Tungsten, Columbium, and Tantalum, DMIC-Memo-49; Battelle Memorial Institute, Defense Metals Information Center; March 31, 1960.
28. Noesen, S. J. and Hughes, J. R.; "Arc Melting and Fabrication of Tungsten", Trans of the Metallurgical Society of AIME, 218, p 259; April 1960.
29. Bridges, W. H.; Metallography Report 349; Union Carbide Corporation-Nuclear Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; July 28, 1960.

APPENDIX

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ANALYTICAL PROCEDURES

PHYSICAL METHODS

Particle Size Distribution (by Micromerograph)

The particle-size distribution of commercial tungsten powders was determined with a Sharples Micromerograph^(f) by the application of Stokes' Law of fall for the velocity of particles rolling in a gas. In this instrument a sample of powder (approximately 0.1 gram) dispersed by dry nitrogen as individual particles is introduced into the top of a polished aluminum sedimentation column (3 1/2" ID x 7' L). The particles fall down the column into a pan of a recording balance located at the bottom. The accumulated weight of powder on the pan is instantaneously balanced by a servo-electronic system containing a restoring torque coil; and the balancing current, which is proportional to the weight on the pan, is read by a recording milliammeter. The recording milliammeter produces a chart which is a record of the current in the restoring torque coil as a function of time and indicates the changes of current fed to the restoring coil to maintain a position of equilibrium for continuously changing conditions of weight on the balance pan caused by the settling particles.

Changes in the record continuously occur as powder particles of smaller and smaller diameter accumulate on the pan until all of the powder has settled. By using a correct form of Stokes' Law it can be shown that the time required for any particular percentage of the powder to settle is inversely proportional to the square of the corresponding particle size in microns (d) and to the density. The information on the chart is used to obtain a complete particle size distribution curve showing the percentage weight of particles smaller than any given micron size. A standard template is used to convert the time scale on the chart into $d/\sqrt{\rho}$. These figures can then be divided by the square root of the density of the particles to get the diameter in microns. The Micromerograph is particularly suited for materials having particles in the range of 2 to 150 microns.

BET Surface Area

At liquid-nitrogen temperatures, nitrogen gas is adsorbed on the surface of a powder. The volume of nitrogen adsorbed by the sample at the liquid-nitrogen temperature is measured at three pressures, and these values are used to make a BET plot using the

(f) The Sharples Micromerograph; The Sharples Corporation, Bridgeport, Pennsylvania.

theoretical concepts of the Brunauer, Emmett, and Teller (BET) theory of gas adsorption.^(g) The volume of nitrogen (STP) forming a monolayer on the surface of the powder is calculated from the BET plot. Since one cubic centimeter of nitrogen (STP) forms a monolayer covering 4.37 square meters, the volume of nitrogen forming a monolayer of gas on the surface of the sample multiplied by 4.37 square meters per cubic centimeter divided by the weight of sample in grams gives the total surface area in square meters per grams. A sample weight of approximately 5 - 10 grams is used for this analysis.

Density by Helium Displacement

The same apparatus used for the determination of BET surface area is used for the determination of density by helium displacement. Whereas the BET surface area procedure provides a measurement of the volume of nitrogen gas adsorbed by the powder sample in a calibrated system of known volume, the helium displacement density procedure provides a quantitative measure of the volume of helium gas displaced by the sample; ie, the sample volume contained in a calibrated system of known volume. From the known weight of sample used and the sample volume, the density may be readily calculated.

Crystallite Size

The crystallite size of tungsten powder was determined by X-ray analysis using the procedure outlined by Klug and Alexander.^(h) The method makes use of the X-ray diffractometer to obtain the line broadening of different diffracted planes of the material being tested. By measuring the width of the broadening at half maximum, the crystallite size can be calculated. For tungsten powder, the 110 and 200 planes are used. If the crystallite size is large, the K_{β} 110 and 200 are used; if the crystallite size is small, the K_{α} 110 and 200 planes are used.

(g) Brunauer, S., Emmett, P. H., and Teller, E.; J Amer Chem Soc, 60, p 309 (1938).

"Determination of Surface Area of Powder by Nitrogen Adsorption Method", Procedure 5.1, K-25 Plant Works Laboratory Manual, K-990; Union Carbide Corporation-Nuclear Division, Gaseous Diffusion Plant, Oak Ridge, Tennessee; January 2, 1953.

Vance, R. F. and Patterson, J. N.; Special Report on Apparatus for Surface-Area Determination and Other Adsorption Studies on Solids; Battelle Memorial Institute; August 1, 1954.

(h) X-Ray Diffraction Procedures, Chapter 9; John Wiley and Sons, New York, NY.

Determination of the Sintered Density

The density of the sintered tungsten metal compacts was obtained by the Archimedian method as follows:

1. Weigh the dry pellet to the nearest tenth of a milligram.
2. Immerse the pellet in dibutyl Carbitol (diethyleneglycol dibutyl ether) and impregnate the pellet under vacuum (~ 24" Hg) for approximately one hour to fill any pores or cracks.
3. Wipe off excess Carbitol from the surface of the pellet with soft paper tissue and weigh to the nearest tenth of a milligram.
4. Suspend the pellet from the balance by means of a fine wire into a beaker of distilled water at a known temperature and obtain the weight while immersed in water.
5. Calculate the density (d) by:

$$d = \frac{W_d \times d_1}{W_i - (W_1 - w)}$$

where:

W_d represents the dry weight in air,

W_i is the weight after Carbitol impregnation,

d_1 is the density of distilled water at the test temperature,

w is the weight of the wire used to suspend the pellet in distilled water, and

W_1 is the weight of the pellet while immersed in distilled water.

CHEMICAL METHODS

Nitrogen (as nitride)

Nitride nitrogen was determined using a modified micro-Kjeldahl method. The tungsten powder or sintered pellet was dissolved in a mixture of nitric and hydrofluoric

acids and the nitride content was hydrolyzed to the ammonium ion. After adding sodium hydroxide and boiling, liberated ammonia was collected in a weak sulfuric acid solution. Nitrogen was determined colorimetrically after adding Nessler's reagent. The lower limit of detection with this method is approximately 20 ppm.

Carbon

Carbon was determined by a conductometric method⁽ⁱ⁾ using a commercial apparatus.⁽ⁱ⁾ The sample was combusted quantitatively with pure oxygen in a high-frequency induction furnace. The amount of carbon dioxide formed was measured conductometrically after it was absorbed in a barium hydroxide solution. The lower limit of detection of this method is approximately 30 ppm.

Oxygen (as oxide)

Oxygen was determined with a Leco conductometric oxygen analyzer (inert gas fusion apparatus). The sample was heated in a platinum bath in the presence of excess graphite and converted to carbon dioxide. The carbon dioxide formed was absorbed in barium hydroxide and measured conductometrically. The lower limit of detection with this method is approximately 5 ppm.

(i) The Determination of Oxygen, Nitrogen, Hydrogen, and Carbon in Molybdenum, Tungsten, Columbium, and Tantalum, DMIC-Memo-49; Defense Metals Information Center, Battelle Memorial Institute, Columbus, Ohio.

(i) Manufactured by the Laboratory Equipment Corporation, St. Joseph, Missouri.