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Refractomet Division

UNIVERSAL-CYCLOPS STEEL CORPORATION

Technical Report

Bridgeville, Pennsylvania

AMC TR 8-107 (1)

AMC INTERIM REPORT 8-107 (1)
April, 1963

DEVELOPMENT OF TUNGSTEN SHEET BY THE USE OF ULTRA-FINE TUNGSTEN METAL POWDER

PHASE I TECHNICAL PROGRESS REPORT

Contract AF33(657)-10513

First Interim Report

28 January 1963 - 28 March 1963

Prepared By

J. H. Schwertz

UNIVERSAL-CYCLOPS STEEL CORPORATION
REFRACTOMET DIVISION
BRIDGEVILLE, PENNSYLVANIA

The State-of-the-Art of ultra-fine tungsten metal powder, its manufacture, consolidation and potential conversion to sheet product is analyzed and evaluated.

BASIC INDUSTRY BRANCH
MANUFACTURING METHODS DIVISION

AMC Aeronautical Systems Center
United States Air Force
Wright-Patterson Air Force Base, Ohio

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April, 1963

Development of Tungsten Sheet By The Use of Ultra-Fine Tungsten Metal Powder

Refractomet Division
Universal-Cyclops Steel Corporation

The State-of-the-Art Analysis of the use of ultra-fine tungsten metal powder (.01 to .1 micron range of particle size) in the production of tungsten sheet products has been completed. Both the available technology and industry capabilities as related to raw material availability, handling methods, consolidation practices and conversion methods have been analyzed. The three major commercial sources of ultra-fine tungsten powder have performed limited experimentation in further consolidation of these powders. Government facilities and private research organizations have made limited investigation of the powder, consolidation and fabrication characteristics.

The State-of-the-Art included a discussion of the recrystallization and ductile to brittle transition temperature behavior of sheet produced from conventional tungsten powders; the significance of these findings to this program is noted.

A program for Phase II of this contract is proposed.

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FOREWORD

This Interim Technical Progress Report covers the work performed under Contract AF 33(657)-10513 from 28 January 1963 to 28 March 1963. It is published for technical information only and does not necessarily represent the recommendations, conclusions or approval of the Air Force.

This contract with the Refractomet Division, Universal-Cyclops Steel Corporation, Bridgeville, Pennsylvania, was initiated under AMC Aeronautical Systems Center Project 8-107, "Development of Tungsten Sheet by the Use of Ultra-Fine Tungsten Metal Powder." It is administered under the direction of Mr. Hugh L. Black, Project Engineer, Metallic Material Branch, Manufacturing and Materials Technology Division, AMC Aeronautical Systems Center, Wright-Patterson Air Force Base, Dayton, Ohio.

Mr. J. H. Schwertz is the Project Engineer in charge at Universal-Cyclops Steel Corporation. Others who co-operated in the research and preparation of this report were: Mr. L. M. Bianchi, Technical Manager and Mr. W. A. McNeish, Assistant Technical Manager.

Since the nature of this work is of interest to many fields of endeavor, your comments concerning the program are solicited.

****

PUBLICATION REVIEW

Reviewed By W. A. McNeish

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I. Introduction

It is a recognized fact that, with the rapid increase in technology in the aircraft, missile and spacecraft industries, the demand for structural materials capable of withstanding the higher temperatures and stress requirements has become critical. The refractory metals offer the most practical approach to solving these problems.

Tungsten, due to its high melting point, high temperature strength and relative abundance with respect to the other refractory metals, has been considered the most promising of this group for future needs. There has been considerable progress made in developing higher quality tungsten sheet, rolled from either vacuum arc cast ingots or sintered powder billets; however, advances in this area have been limited due to temperature, atmosphere and/or equipment limitations. There are also several programs currently in progress to increase the size and improve mechanical properties of tungsten sheet. It is the objective of this program to produce defect-free, high formability tungsten, flat rolled sheets via ultra-fine tungsten powder, an inert working atmosphere and high fabrication temperatures.

This program involves five phases to run in chronological order as follows:

Phase I - State-of-the-Art Analysis
Phase II - Procurement and Initial Processing of Powder
Phase III - Development of Optimum Sintering Procedures
Phase IV - Breakdown and Initial Rolling of Tungsten Billets
Phase V - Minimum Pilot Sheet Production

This first interim report covers the work of the Phase I efforts.

II. Phase I - State-of-the-Art Analysis

A. General Procedure

The objectives of the analysis were to explore the current State-of-the-Art of ultra-fine tungsten powder and its final

conversion to sheet product and to recommend the necessary controls and processing to evaluate the existing commercial ultra-fine powders.

In conducting the analysis, use was made of a questionnaire, an extensive search of the literature was made and the Defense Metals Information Center was visited. The questionnaire used is reproduced in Appendix B to this report; approximately 236 copies were sent to organizations that were known or believed to have worked with tungsten or tungsten alloys in any stage of processing. Personal contacts were made with a number of organizations which have been actively engaged with ultra-fine tungsten powder. The complete list of organizations contacted is given in Appendix C to this report.

The data collected was of two types. That information which updated the State-of-the-Art survey prepared on Air Force Contract Number AF 33(600)-41917 and that pertaining only to ultra-fine tungsten powder. The former data will be covered first.

B. Tungsten Powder Greater than 1.0 Micron

1. Raw Materials

In the present technology of tungsten, the source of all commercial tungsten product is tungsten powder. The processing of the ore to finished powder has been discussed by several authors[1,2,3]. There are various methods for the final reduction step to powder, but the accepted method for commercial powder, from a high purity standpoint, is the reduction, by hydrogen, of either the oxide (WO_3) or ammonium paratungstate. The paratungstate is an intermediate step in the preparation of the oxide but can be directly reduced to the metal powder. Generally speaking, the paratungstate will be more dense and will have a larger and more uniform particle size than the oxide.

The major producers and/or suppliers of tungsten powder in the United States at the present time are as follows:

Climax Molybdenum Company
Fansteel Metallurgical Corporation
Firth Sterling, Inc.
General Electric Corporation
Kennametal, Inc.
M & R Refractory Metals, Inc.
Reduction and Refining Company
Shieldalloy Corporation
Sylvania Electric Products, Inc.
Union Carbide Metals Company
Vitro Laboratories
Wah Chang Corporation

2. Particle Size

Tungsten metal powder is produced commercially in a wide range of particle sizes. The ultra-fine powders (0.01 to 1.0 micron size) will be covered in detail further on in the report. The large particle size powders (1.0 micron and larger) are used for a variety of specialized applications ranging from spray coating for the finer sizes to laboratory tooling for high purity, ductile single crystals[4]. However, for the majority of commercial applications, the particle size range of 1.0 micron size to 10 micron size is preferred. This size range lends itself most readily for consolidation to fabricable shapes and to consumable-electrode stock. Control of this particle size depends on a number of variables such as the size and purity of the original oxide or paratungstate, the reduction cycles, the quantity of powder being reduced and its proximity to the hydrogen reductant, and the flow rate, purity and water vapor content of the hydrogen reductant.

Particle size distribution also plays an important role in the consolidation of tungsten shapes. Usually, this distribution is controlled by close control of the reduction variables. However, in order to acquire a definite particle size and distribution characteristics, various

lots are sometimes blended together as a commercial practice.

The most common methods of measuring particle size distribution are: (1) Photolometer-light transmission during a sedimentation process; (2) Micromerograph - velocity of fall in N_2; and (3) Microscopic count. There has been very little published data on the effect of grain size disbribution on consolidation, this being considered proprietary information by most producers. Table I[5] shows particle size distribution of three high purity, hydrogen reduced tungsten powders that are supplied for effective consolidation results.

3. Purity

As previously stated, high purity tungsten powder is generally hydrogen reduced. Purity levels of over 99.95% are obtained with the major impurities being oxygen and nitrogen. To a limited extent, pure tungsten is produced by the reduction of tungsten hexachloride[6,7] or tungsten hexafluoride[8]. Average analyses obtained in the reduction of the hexafluoride is given in Table II. The total impurity content by this process is less than 100 parts per million.

The response to the questionnaire in regard to purity specifications, has been rather spasmodic but the available information has been tabulated in Table III. It is noted from these limits that the elements of most concern are oxygen, nitrogen, carbon, nickel, molybdenum, iron and silicon. The rather wide variation of these elements between producers and consumers indicates the lack of knowledge of the effects of specific impurities on fabricability and mechanical properties and the difficulties encountered in analyses of the metal powder, especially for the interstitial elements of oxygen, nitrogen and hydrogen.

TABLE I

Particle Size	Weight Per Cent Particles of the Indicated Size (by Photolometer)		
MICRONS	LOT A	LOT B	LOT C
< 1	5.0	1.5	.3
1	31.8	1.5	.3
2	39.3	8.2	3.1
3	21.1	17.9	7.6
4	2.1	22.0	10.4
5	.6	19.4	19.5
6	.1	13.2	9.4
7	--	7.4	7.3
8	--	5.0	6.4
9	--	3.7	4.8
10	--	1.6	4.0
11	--	--	3.6
12	--	--	3.6
13	--	--	3.3
14	--	--	3.1
15	--	--	1.3
20	--	--	2.5
25	--	--	1.8

TABLE II

Analysis of Tungsten Made By Hydrogen Reduction of WF_6 (8)

Impurity	Average of 5 samples Wt. %
Aluminum	.0008
Calcium	.0002
Copper	.0003
Iron	.0004
Magnesium	.0010
Manganese	.0003
Nickel	.0005
Silicon	.0028
Molybdenum	.0001
Carbon	.0015
Oxygen	.0010
Hydrogen	.0002
Nitrogen	.0000
TOTAL	.0091

TABLE III

Current Purity Specifications for Tungsten Powder

Company or Organization	W	Impurity Content Weight Per Cent									
		O max	N max	C max	Al max	Ca max	Fe max	Mo max	Na max	Ni max	Si max
Producers											
Firth Sterling	99.9	.03	--	.005	.002	.002	.002	.005	--	.002	.002
General Electric	99.90	.03	.015	.003	.001	.001	.005	.005	.001	.001	.003
Kennametal	99.75 min	.05	--	.005	.005	.005	.02	.100	.005	.005	.020
Shieldalloy	99.95 min	.01*	.001	.003	Trace	.003	.006	.010	.002	Trace	.001
Sylvania Electric	9 .95 min	--	--	.005	.005	.003	.002	.005	.002	.002	.001
Wah Chang	Balance	.10	--	.005	.002	.005	.005	.01	.005	.01	.005
Consumers (Powder)											
Clevite Corporation	Balance	.006	--	.001	.003	.001	.001	.026	.003	.001	.001
General Chemical Div. (Allied Chemical Corp.)	99.90 min	.050	.005	.005	.002	.002	.002	.005	.002	.002	.002
Consumers (Sintered Shapes)											
Cameron Iron Works	Balance	.003	.002	.003	--	--	.002	--	--	--	.002
Ladish Company	99.95 min	.006	.005	.010	.005	.001	.010	005	--	.005	.005
Lockheed Missles & Space Company	--	.020	.020	.030	--	--	.050	.250	--	--	.050
Universal-Cyclops (Electrode Stock)	--	.010	.0025	.0025	.001	.003	002	.005	.003	.001	.001

* - Depending on Particle Size

4. Compacting

Until recent years, the pressing of tungsten powders has been primarily accomplished by cold compaction utilizing simple mechanical pressing techniques. This method is limited to relatively small rectangular or cylindrical shapes formed by uniaxial compression of the powder in steel dies. The product lends itself readily to further fabrication by sintering, swaging and drawing into rods and wire. Small slabs for further fabrication into sheet product also have been made by this method. In some cases, to give a more uniform pressure gradient through the piece, a double action pressing operation is used where the top and bottom plungers of the die assembly are free to move with respect to the die wall.

Hot pressing has been used to some extent to consolidate larger size tungsten shapes. This method utilizes a combination of temperature and pressure where the tungsten powder is plastically deformed to give a high density sintered product in one operation. However, due to the high temperatures necessary, this method requires the use of carbon or graphite molds and the contamination of the tungsten by carbon to form carbides on the surface of the part presents serious problems. More commonly, this method is used to consolidate the larger sizes of WC-Co cemented carbide compositions.

In recent years, explosive compaction of tungsten powders has received considerable attention. Battelle[9] reports that it is possible at ambient temperatures to explosively compact tungsten powders to 95% of full density. Explosive forming of tungsten nozzles using rolled and welded sheet tubes in an aluminum bath at 1800°F. is of current interest for making asymmetrical nozzle shapes.

A method of consolidation which has recently been applied to tungsten powders on an experimental basis is gas

pressure bonding[10]. Tungsten powder is first cold pressed into shape, then sealed in an evacuated metal envelope and heated under gas pressure. In preliminary trials it has been possible to produce densities of 95 to 98% of theoretical by heating canned compacts at 2700°F. in a pressure chamber for three (3) hours under isostatic gas pressures of 10,000 psi.

The most important advancement in recent years to powder compacting has been the use of isostatic pressing. In this process tungsten powder is loaded into a plastic or rubber bag of appropriate size and geometry. The bag is sealed and placed in a pressure chamber and the chamber is filled with a fluid medium and subjected to hydraulic pressure. The use of isostatic pressing has allowed the preparation of massive tungsten shapes with much improved density gradients throughout the cross section. Commercial facilities now exist capable of producing rounds in the neighborhood of 14" diameter by 15 feet long. Electrodes for use in vacuum arc melting to tungsten ingots have been prepared in this manner along with sheet bar in the size range of 1-1/4" x 10" x 17" for direct rolling to sheet and plate product. Densities obtained by this method range from 50 to 75% of theoretical with most falling into the range of 60 to 65%. Pressures commonly used vary from 30,000 to 50,000 psi.

Isostatic pressing has permitted the compacting of shapes that were previously very difficult to obtain by mechanical methods. These shapes include large cylinders, rings, tubes, rocket-nozzle-throat shapes, vanes and other contoured sections.

5. Sintering

The sintering operation, with respect to tungsten powder compacts, performs two distinct and important operations. (1) It purifies the pressed compact by the reduction of

residual oxygen by hydrogen and (2) it densifies the compact to a form where it has sufficient strength to be applied directly as finished product or to be sufficiently workable as to be further fabricated to wrought products. Sintering of tungsten shapes is based on a solid state diffusion process and optimum results are dependent on a number of factors including initial powder purity, particle size, compacting pressure, and sintering time and temperature. A. R. Poster[11] has made a detailed investigation of these factors on maximum sintered properties and Agte and Vacek[3] have also discussed the effect of powder properties on sintering behavior. Among the effects noted were the following:

a. Although finer powders compact less easily, they tend to sinter more readily.

b. High purity aids in the consolidation rate.

c. Particle size distribution is an important factor in consolidation.

d. Final sintered density is pressure-independent within a wide range of pressures.

e. Sintering temperature is the most important factor in final consolidation.

Figure 1[3] illustrates the influence of sintering temperature on densification of cold compacted tungsten powders. The specific time-temperature combinations used to sinter tungsten are considered proprietary by most organizations but would depend on the end use of the compacts as well as the facilities available for sintering.

Pugh and Amra[12] have investigated the effect of vacuum sintering on the density, purity and grain size of tungsten. Figure 2[12] indicates the effect of temperature on sintered density for various times at temperature. The

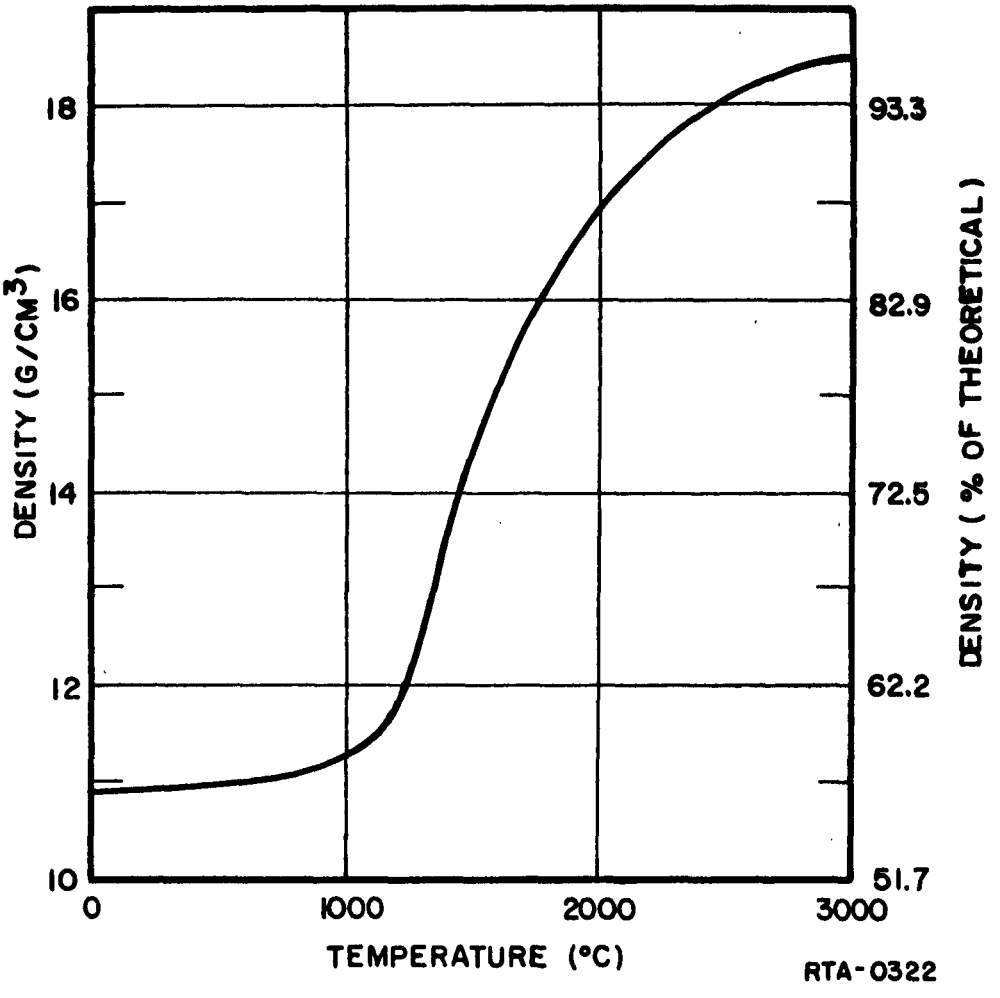

FIGURE 1

INFLUENCE OF SINTERING TEMPERATURE ON THE DENSITY OF PURE TUNGSTEN BARS SINTERED FOR 1/2 HOUR

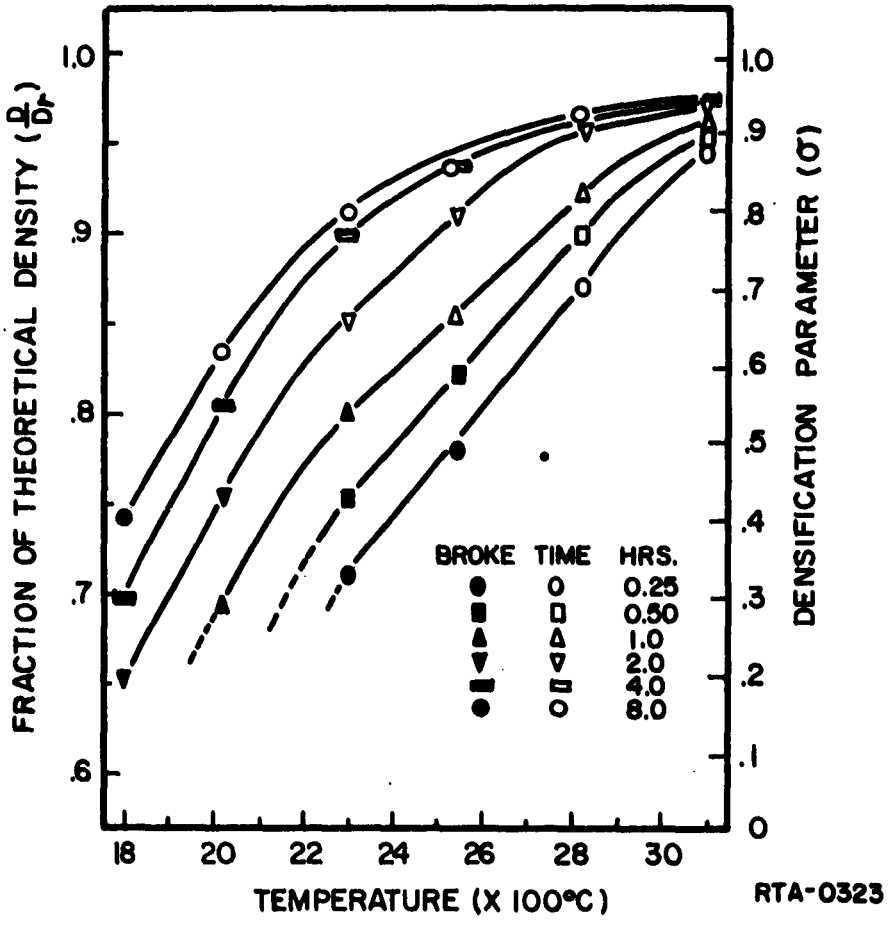

FIGURE 2

EFFECT OF TEMPERATURE ON THE DENSIFICATION OF TUNGSTEN INGOTS

solid data point symbols in Figure 3 represent ingots which could not be swaged satisfactorliy. Prom these curves it is apparent that the ingot must attain more than 82.5% of its theoretical density before it can be fabricated in this manner.

In general, for fabrication of the larger shapes to finished mill products, densities of 90-95% of theoretical are necessary. For electrode stock, densities of 82-90% have proved satisfactory.

6. Doping Additions

A number of suppliers are using doping additions to the starting tungsten oxide in the form of solutions of soluble salts. Although the additions are considered proprietary by most suppliers, generally, they consist of mixtures of alkaline oxides with silica and/or alumina. The major purpose of these doping additions is to produce an abmornal or interlocking elongated grain structure in the recrystallized metal. The structure, due to the increased grain boundary area, tends to reduce offsetting at high temperatures due to grain boundary shear. This is especially effective in the tungsten filament industry where the principle is used to develop non-sag wire. Some of the mixtures that have been used with respect to filament wire are listed in Table IV[3]

Bodine[13] has included doping additions in his investigations under the Navy Sheet Rolling Program. Some of the mixes investigated were:

a. Alkali-silicate doped tungsten powder prepared by single stage hydrogen reduction of doped tungstic acid.

b. Alkali-silicate-aluminum doped tungsten powder prepared by single stage hydrogen reduction of doped tungstic acid.

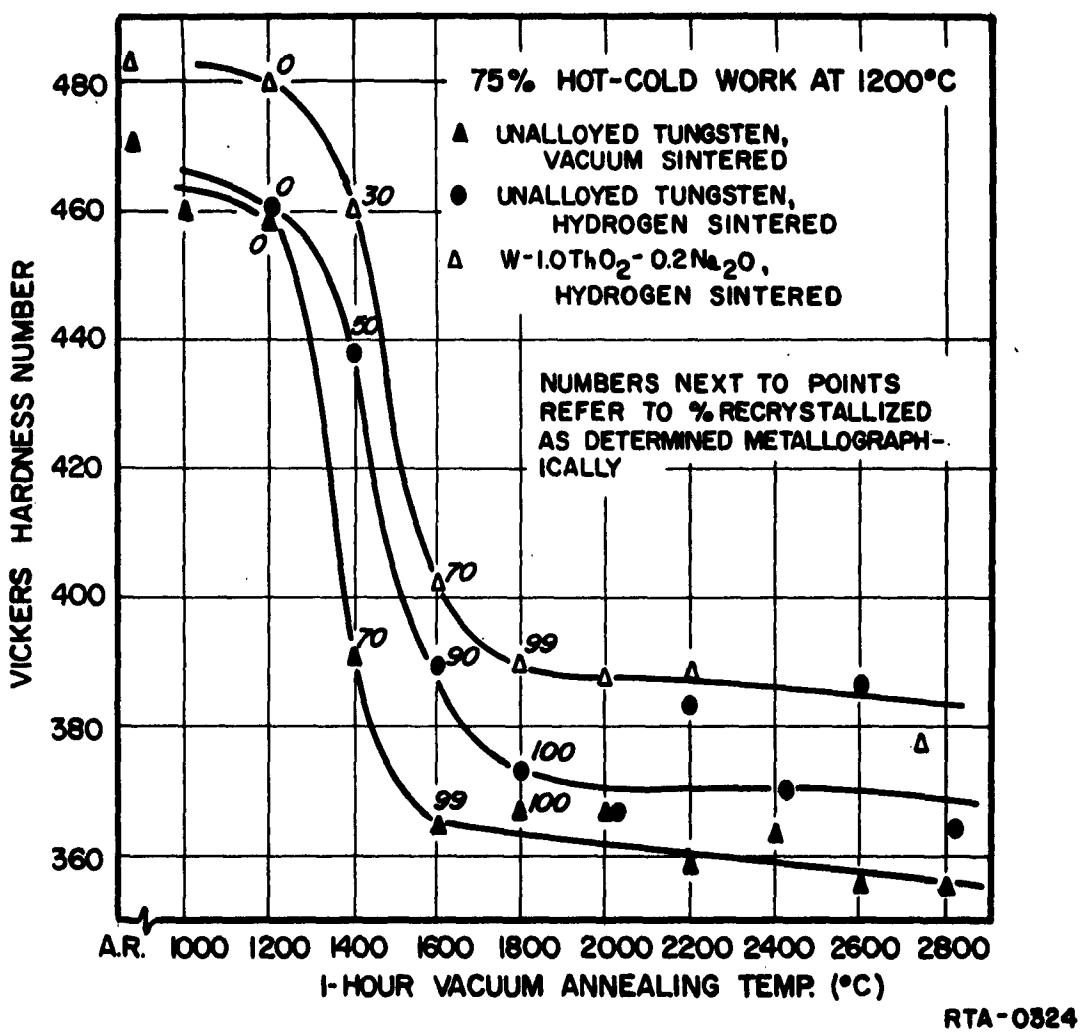

FIGURE 3

SOFTENING CURVES FOR WROUGHT POWDER-METALLURGY TUNGSTEN COMPARED WITH THAT OF W-1.0ThO_2-0.2Na_2O (AQUEOUS ADDITIONS)

TABLE IV

Typical Dopes Added to Influence Recrystallization In Tungsten Wire[3]

(Expressed as Percentage WO_3)

0.45%	K_2O,	0.20%	SiO_2		
0.35%	K_2O,	0.30%	SiO_2		
0.15%	K_2O,	0.25%	Na_2O,	0.24%	SiO_2
0.15%	K_2O	0.10%	SiO_2,	0.04%	Al_2O_3
0.15%	K_2O,	0.24%	SiO_2,	0.05%	Al_2O_3
0.145%	K_2O,	0.30%	SiO ,	+0.025%	Al_2O_3

(The latter added to reduced powder.)

0.15%	K_2O,	0.15%	SiO_2,	and up to 0.1% CaO

c. Alkali-silicate doped tungsten powder containing 0.1% carbon addition.

d. Tungsten powder hydrogen reduced from a blend of equal portions of alkali-silicate doped tungstic acid and undoped tungstic acid.

e. Alkali-1% thoria doped.

Preliminary results of his investigations indicated that the alkali-silicate-aluminum doped powder and the alkali-1% thoria doped powder warranted further study due to (1) sintered density and sheet properties were promising on the former powder and (2) elevated temperature sheet properties were superior with reasonable working and fabrication properties on the latter. However, on recommendations of the MAB, work was continued only on undoped tungsten powder due to equipment problems (condensation of volatile phases) in connection with the doped powders.

While the conventional doping additions are usually volitalized during the sintering operation, there have been recent investigations into the more stable despersoid additions and their effect on fabricability, recrystallization behavior and ductile-brittle transition temperature with a view toward increasing the low temperature ductility of tungsten as a sheet material. R. I. Jaffee et al[14] have made an extensive study of the effect of these additions on the recrystallization and ductile to brittle transition behavior of tungsten with some very interesting results. The most promising of these additions were ThO_2, ThO_2-NaO_2 combinations and ZrO_2. For uniformity of results, the additives were made to the tungsten powder rather than the usual method of adding to the oxide. The results of primary recrystallization temperature determinations on the ThO_2, ThO_2-Na_2O and ZrO_2 additions indicated that the recrystallization temperature of tungsten was increased as much as 100-200°C. and resulted in the forma-

tion of elongated grains. Figure 3[14] compares the softening curves for wrought powder metallurgy tungsten compared with that of W-1.0 ThO_2-0.2Na_2O (aqueous additions).

Rolled and annealed tungsten-base powder metallurgy dispersoid alloys were investigated for ductile brittle transition behavior in bending. The dispersion additions were expected to restrict grain growth, thereby reducing the effect of the density of grain boundary impurities and giving an elongated grain structure characteristic of favorable ductility. Moreover, according to Petch[15], a reduction in grain size would effectively lower the transition temperature by increasing the fracture stress and plastic strain before fracture. Table V[14] gives the ductile-brittle transition temperature of 75% hot-cold rolled and annealed tungsten and tungsten dispersoid alloys. In general, the effect of the additions were a 30-80°C. (86-176°F.) lowering of the transition temperature.

The effect of grain size on the bend transition temperature is indicated in Figure 4[14]. ThO_2 additions effectively decreased the bend transition temperature of recrystallized tungsten by as much as 50°C. Also, the effect of recrystallized grain size is very noticeable with the smaller grains giving much lower transition values. The effects noted with ZrO_2 were very similar to those reported with the ThO_2 additions.

The effect of the particle size of the dispersoid addition has been noted by Jaffee et al[14] on the transition temperatures. The finer the particle size of the addition, the lower the transition temperature. Cremens[16] work on elevated temperature properties of nickel powder extrusions containing dispersions of aluminum oxide has led

TABLE V

Ductile-Brittle Transition Temperature of 75% Hot-Cold Rolled and Annealed Tungsten and Tungsten - Dispersoid Alloys[14]

Alloy	As-Wrought and Annealed One Hour at 1200°C. 10T Transition Temperature °C.
Unalloyed Tungsten	230
W-1.0ThO_2-Na_2O (Aqueous+NaCl)	180
W-1.0ThO_2-Na_2O (Aqueous+Na_2CO_3)	190
W-1.0ThO_2-0.5Na_2O (Aqueous+NaCl)	240
W-1.0ThO_2-0.2Na_2O (Aqueous+NaCl)	200
W-1.0ThO_2 (Aqueous)	160
W-1.0ThO_2 (3.0 micron size)	290
W-0.12ZrO_2 (.01 micron size)	200
W-0.60ZrO_2 (.01 micron size)	150
W-3.20ZrO_2 (.01 micron size)	180
W-0.60ZrO_2 (Aqueous)	200
W-0.60ZrO_2 (1.9 micron size)	200
W-0.53ZrO_2 (Stabilized 3.1 micron size)	190

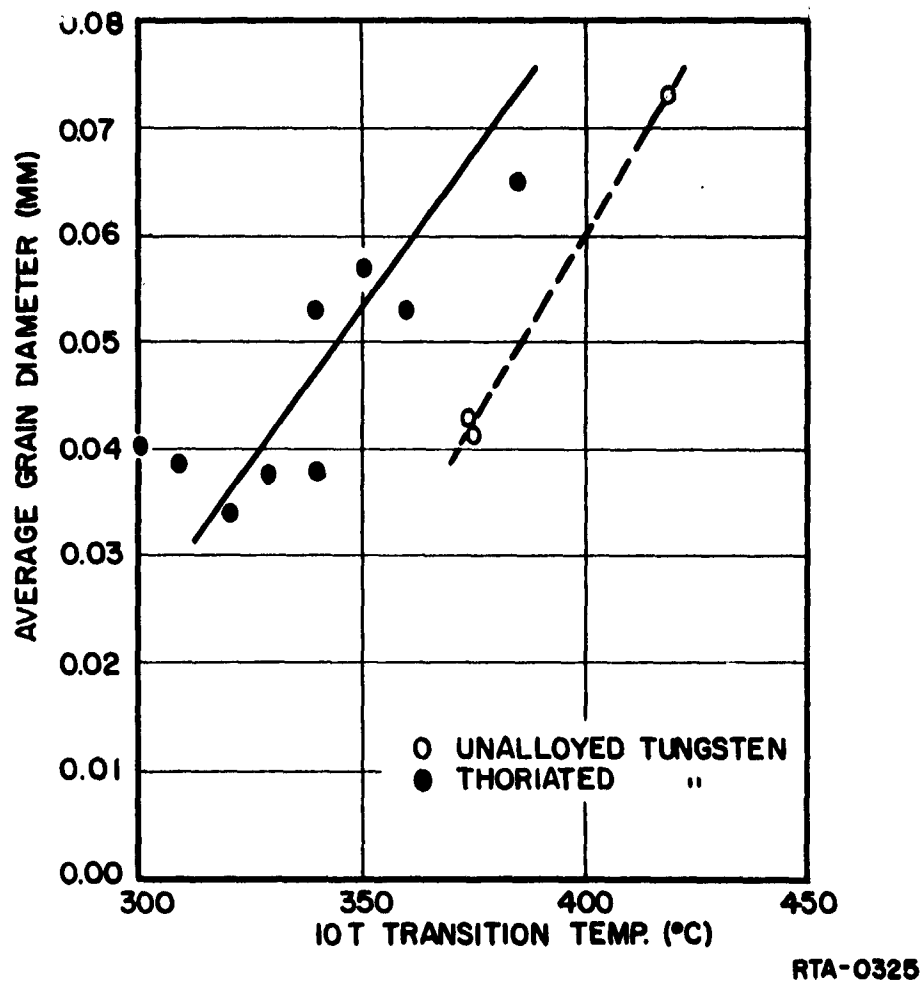

FIGURE 4

EFFECT OF GRAIN SIZE ON THE BEND TRANSITION TEMPERATURE OF RECRYSTALLIZED TUNGSTEN AND THORIATED TUNGSTEN ALLOYS WITH AND WITHOUT Na_2O ADDITIONS

to the proposition that high temperature rupture strength increases as inter-particle spacing decreases and maximum strength values are to be expected only with inter-particle spacings less than 1 micron. The consideration of dispersoid additions to the sub-micron tungsten metal powder, based on this work, would be strongly recommended.

7. Conversion Practice

Battelle Memorial Institute has completed a State-of-the Art survey for Universal-Cyclops Steel Corporation on Contract AF 33(600)-41917[17] in which the current capability of industry for conversion to tungsten sheet is covered in detail.

In general, the present commercial practices of producing tungsten sheet are regarded as proprietary and very little information was obtained by the survey questionnaire. Currently, powder metallurgy techniques are being used to produce commercial sheet product. Universal-Cyclops[17], on its arc-cast tungsten sheet rolling program, has produced approximately 36" x 36" arc-cast sheet and is currently scaling-up to the program objectives of high purity sheet 36" x 96".

In the past, tungsten strip for the electronics industry has been produced from mechanically pressed and resistance sintered sheet bar approximately one to two square inches in length. This size is considered the maximum that can be economically sintered by direct resistance. Due to the increased demands for larger sections of sheet and plate product, the producers are resorting to the use of isostaticly pressed sheet bar in much larger sizes than before. Sintering facilities have been scaled-up to handle more massive shapes at appropriate temperatures. It is generally accepted that close grain size control is necessary for direct rolling of tungsten sheet bar, and,

to accomplish this, long time, low temperature sintering cycles are recommended.

For direct rolling applications, desirable density ranges fall between 88 to 95% of theoretical with the most desirable being in the neighborhood of 94%. Some proprietary work is being done on forging and extruding of tungsten stock to sheet bar configuration prior to the initial breakdown rolling.

Most producers of sheet bar and plate and sheet products advocate initial breakdown reductions of 15-25% on the first pass, with some suggesting as much as 50% reduction. This is followed by lesser reductions and lower temperature rolling in the intermediate and final rolling stages. Initial breakdown temperatures range between 2700°F. to 3000°F. from a hydrogen atmosphere furnace, if such equipment is available.

At present, the sheet size limitations vary considerably from producer to producer, depending on available equipment. The largest sizes are advertised by Rembar, (U.S. distributor for Metallwerke Plansee). They have recently installed a 120 centimeter mill capable of producing 40" wide sheets up to 60" long at approximately .020" gauge. Domestic sheet product is available up to 24" wide at .020" gauge.

In regard to the ultra-fine tungsten program, rolling schedules will follow the recommended schedules developed under the Fansteel-Navy Sheet Rolling Program and the Universal-Cyclops-Air Force Sheet Rolling Program, both of which are nearing completion.

8. Properties of Tungsten

Established data on the properties of tungsten have been available for quite some time based on the use of this

metal in the lamp and electronic tube industries. However, this data has been primarily generated on wire product and very little has been generated on other product forms. In recent years attempts have been made to rectify this situation, primarily by government sponsored research. Since the data on wire product has been fairly well established, the information presented will be confined to the more recent work.

A review of the more recent work on sintered tungsten metal product indicates that many of the properties generated are sensitive to processing variables. This makes it quite difficult to directly compare the results of various investigations. However, existing data will be presented with emphasis on sheet properties.

a. Physical Properties

Selected physical and thermal properties for unalloyed tungsten are listed in Table VI. The most unique characteristics of tungsten are its high melting point, high density and low linear coefficient of thermal expansion.

TABLE VI

Selected Physical Property Data
For Unalloyed Tungsten[15]

Melting Point, F	6170
Boiling Point, F	9900
Density, lb/in^3	0.697
g/cm^3	19.3
Crystal Structure	Body-centered-cubic
Lattice Parameter, A°	3.158(3)
Specific Heat, cal/g C	20 C (70 F): 0.033 1000 C (1830 F): 0.041 2000 C (3630 F): 0.047

Thermal Conductivity cal/sec/cm/C	20 C (70 F): 4.43 1000 C (1830 F): 5.17 2000 C (2910 F): 7.24
Linear Coefficient of Expansion; 10^{-6}	20 C (70 F): 4.43 1000 C (1830 F): 5.17 2000 C (2910 F): 7.24

b. Hardness and Recrystallization Behavior

The recrystallization temperature of tungsten is dependent on a number of factors, but the most critical seem to be the degree of cold work and metal purity. In the as-wrought condition the hardness of tungsten sheet or strip can range from 450 to 520 VHN, depending on the amount of hot/cold work in the material. The hardness decreases gradually with increasing annealing temperature to approximately 1200°C. then drops rapidly through the temperature range of 1200 to 1800°C. and finally levels off at higher temperatures to 360 to 380 VHN.

Data generated by Universal-Cyclops and Fansteel on their respective tungsten sheet rolling programs indicate that the primary recrystallization temperature is lowered with increasing amounts of hot/cold work. This is substantiated with results found on tungsten rod and wire. Experimental work at Battelle[5] shows the recrystallization behavior of 50 and 75% hot/cold worked strips (Figure 5). Microstructures of the 75% worked strip indicate a primary recrystallization temperature of 1600 to 1700°C. Vacuum sintered material gave a value of about 1600°C. and the hydrogen sintered a value closer to 1700°C.

Grain size counts were made on both types of recrystallized material and are represented graphically in Figure 6. For both materials, grain size increased by a factor of about 2 as the annealing temperature was

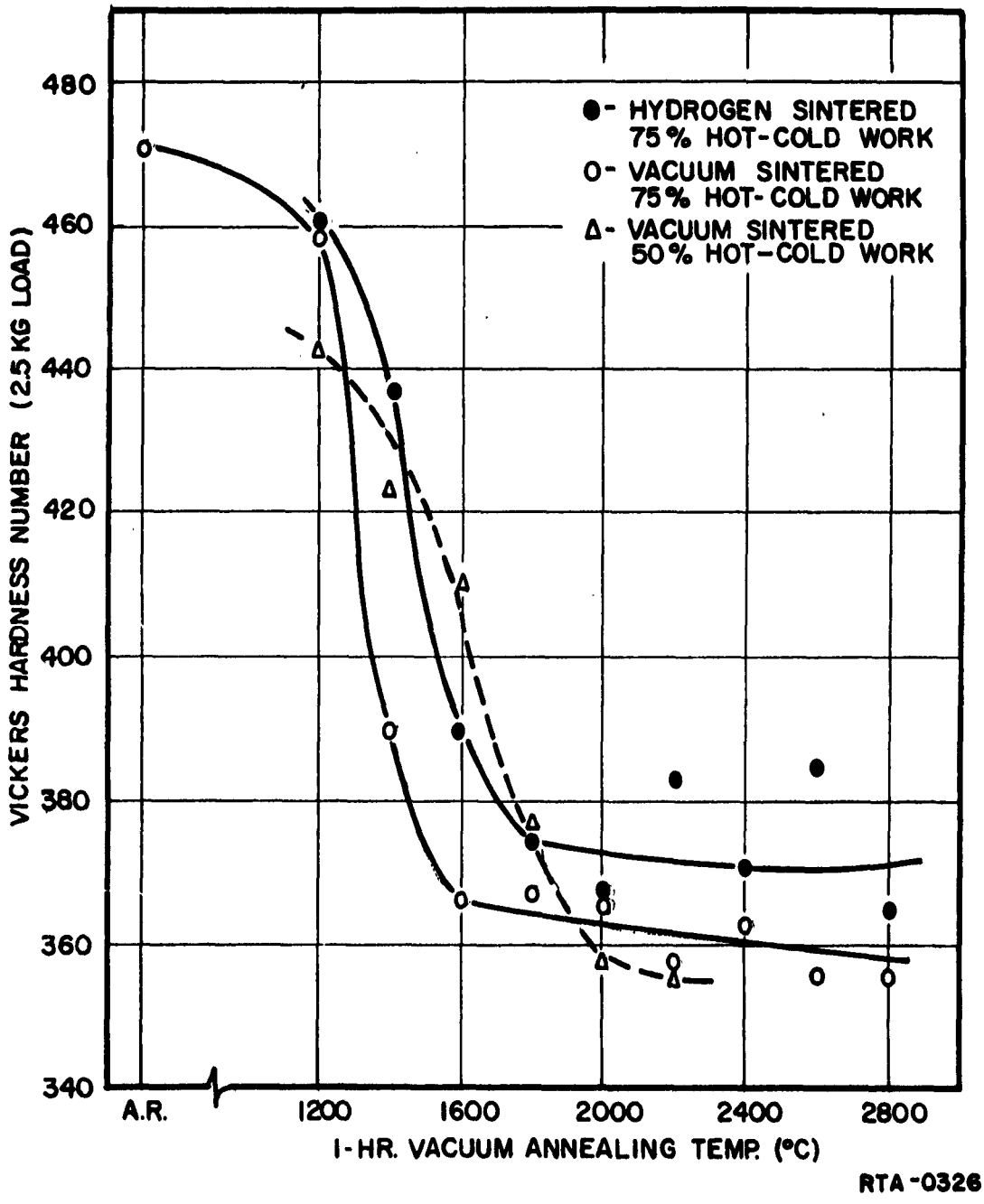

FIGURE 5

SOFTENING CURVES FOR UNALLOYED POWDER-METALLURGY TUNGSTEN

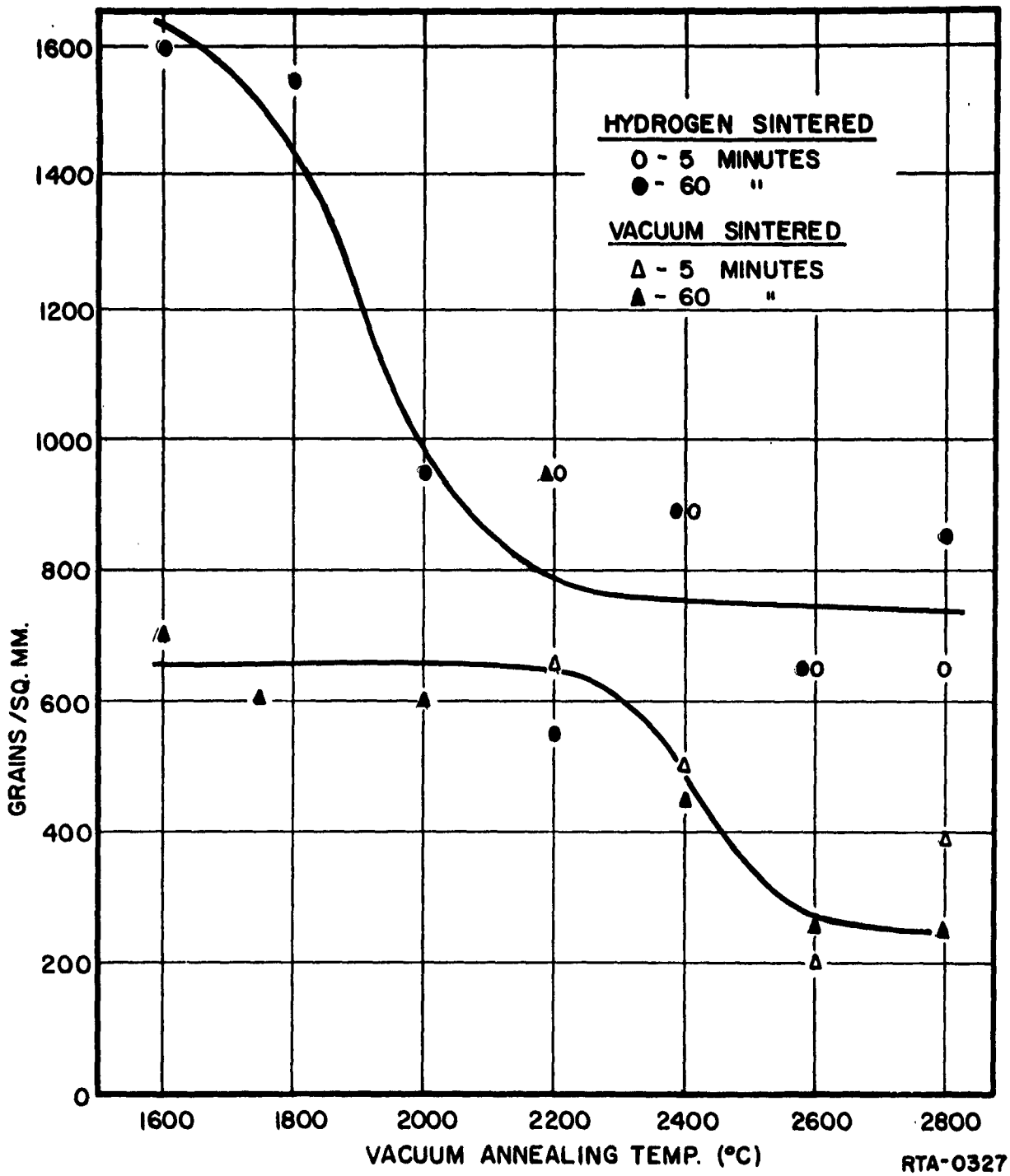

FIGURE 6

GRAIN-SIZE BEHAVIOR OF WROUGHT (75 %) POWDER METALLURGY TUNGSTEN AS AFFECTED BY ANNEALING TEMPERATURE AND TIME

increased from 1600°C. to 2800°C. At 2200°C. and above, recrystallization was complete within five minutes. Increasing annealing times from five to sixty minutes at a given temperature resulted in no significant difference in grain size. However, much finer recrystallized grain sizes were obtained in the hydrogen sintered material. Since the interstitial impurity levels of both sintering mediums were approximately equal, the difference in grain size is attributed to a slightly greater purification of the metallic impurities on vacuum sintering.

c. Ductile to Brittle Transition Behavior

The transition from ductile to brittle behavior is very pronounced in the body-centered cubic metals. In tungsten, this behavior is of vital interest because the transition temperature is above room temperature in almost all finished product.

The ductile-brittle transition temperature may be defined as the temperature (or temperature range) below which the metal fractures with little or no plastic deformation. The accepted theory, based on the work of Cottrell[16], is explained in detail along with a comprehensive study of the "Ductile to Brittle Transition in the Refractory Metals," DMIC Report Number 114[17].

Room-temperature ductility can be achieved in small diameter wire due to the extremely high degree of cold work. This degree of work is not attainable in more massive shapes of tungsten product and all plastic deformation must be conducted at elevated temperatures to avoid brittle behavior. Industry is currently striving to lower this transition behavior so that room temperature deformation can be realized on tungsten sheet product.

The ductile to brittle transition temperature of tungsten has been shown to be sensitive to a number of factors including grain shape and size, strain rate and metal purity. Elongating the grain through cold working decreasing grain size or strain rate, or improving metal purity all tend to lower the transition temperature.

The transition temperature in tungsten sheet is usually determined by bend tests. Universal-Cyclops and Fansteel, on their tungsten sheet rolling programs, have developed considerable data on tungsten sheet. Fansteel[13] has preliminary data which indicate values as low as 100°F. with controlled processing cycles. Work has been done at Battelle on the "Effect of Impurities on the Properties of Tungsten" which give bend ductility data as shown in Figure 7. The graph indicates that the wrought structure is approximately 150 to 200°C. lower in transition temperature than the recrystallized material. The same work by Battelle found that inert dispersed oxides can lower the bend-transition temperature of tungsten strip, primarily through grain-size control, in both the wrought and recrystallized conditions. The lowest bend-transition temperatures observed were obtained with binary additions of 1 per cent ThO_2 and .6 per cent ZrO_2.

Sutherland and Klopp[18], in a study of products from five commercial tungsten sheet manufacturers, found that the bend transition temperature varied from approximately 325°F. to 725°F. between manufacturers. Also, they noted an increase in transition temperature with increasing hydrogen and oxygen content of the five samples.

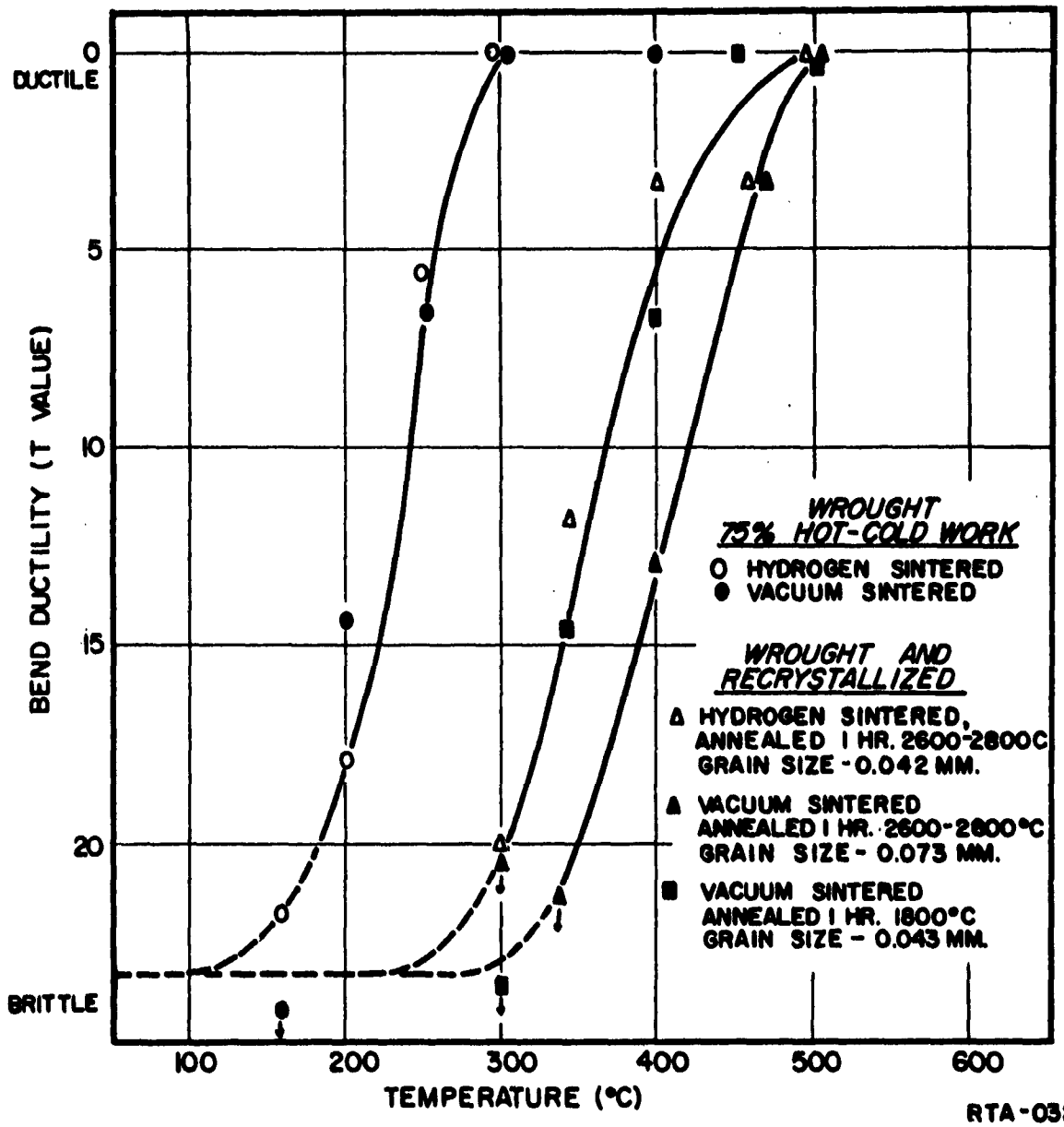

FIGURE 7

BEND DUCTILE-BRITTLE TRANSITION BEHAVIOUR OF WROUGHT AND RECRYSTALLIZED UNALLOYED TUNGSTEN

The effect of surface condition on the ductile to brittle transition temperature of tungsten has been studied by Stephens[19] with the result that the type of defect rather than the average degree of roughness is the principle factor in raising the transition temperature. Sedlatschek and Thomas[20] have found that electropolishing has improved the transverse bend and tensile properties of wrought tungsten. The removal of surface layers of tungsten specimens resulted in appreciable improvements in strength.

d. Mechanical Properties

Until very recently, mechanical properties on tungsten sheet product has been scarce. In the last two to three years, a number of detailed investigations have been made in this area. Hughes Tool Company[21] has issued a summary report on Mechanical Properties of Tungsten in which the quality of commercially available tungsten sheet was investigated. For the initial quality control phase, hardness, microstructure, chemical impurities, flexural properties and tensile strength were determined on material from three sources. Based on these test results, a sepcification requiring high quality material with high cold reduction, was formulated. For the next phase of testing, three powder lots of tungsten sheet, per the specification, were procured from five sources. The tensile test results on this material are presented for room temperature, 1000°, 2000°, 3600° and 4400°F. The material from one producer consistently displayed a limited amount of plastic elongation at room temperature.

Sutherland and Klopp[18] investigated the mechanical properties of five typical commercial lots of tungsten sheet at high temperature. The lots varied significant-

ly from one lot to the other in stress-rupture properties at 4800°F. and tensile properties at 3640°F. to 5270°F. Twofold variations in rupture strengths and tensile strengths were observed.

Barth[15] has made a rather complete summary of present data in DMIC Report Number 127 on the "Physical and Mechanical Properties of Tungsten and Tungsten-Base Alloys."

Ratliff and Ogden[22] have compiled the results obtained from seventeen (17) investigations in which the tensile properties of tungsten have been evaluated, and reported these findings in DMIC Memorandum 157.

No attempt will be made in this report to consolidate the previous mentioned data sources due to the completeness of the coverage already referenced. In general, at temperatures up through 2500°F., the tensile strength of tungsten appears quite sensitive to processing variables, e.g., type of consolidation method and degree of cold working. At 2500°F. strengths from 25,000 to 50,000 psi have been reported. With increasing temperatures, the effect of processing variables on tensile strength appears less marked, and above about 3500°F., the ultimate strength of unalloyed tungsten appears to be essentially independent of both the consolidation practice used and prior thermal history.

C. Tungsten Powder Less than 1.0 Micron

1. General

The effect of grain size on the mechanical properties of metals has been reported by numerous authors[23,26,27]. In general, a finer grain size is accompanied by an increase in hardness, yield strength and fracture strength with a

corresponding decrease in the ductile to brittle transition temperature. Other authors[24,28,29] have indicated that finer grain structure is the key to improving the properties of dispersoid-strengthened metal and alloy systems.

The present theories predict that the maximum mechanical benefits should be found in wrought tungsten products produced from powders having particle sizes much smaller than that which is commercially available. Investigations have been recommended to determine the effect of ultra-fine tungsten powder on mechanical properties of tungsten sheet. (Ultra-fine powder is generally classified as powder in the particle size range of .01 to 0.1 micron in diameter.)

2. Methods of Production

The results of the survey questionnaire indicate that there are approximately six (6) commercial producers of sub-micron tungsten powder and only three (3) that actually produce the powder in the ultra-fine range. Table VII shows the organizations and the particle size of powder produced.

In addition to the above commercial sources, Battelle Memorial Institute has produced 0.2 micron on an experimental basis by the hydrogen reduction of a suspended cloud of WO_3 particles.

The Bureau of Mines, Albany Metallurgy Research Center, has produced 0.001 micron and 0.03 micron powder on an experimental scale by the vapor phase reduction of WCl_6 with H_2. At present, various techniques are being studied for the purification of WCl_6 and subsequent preparation of the tungsten powder.

Lambdin and Perry[30], Oak Ridge Y-12 Facility, Union Carbide Nuclear Company, have developed a continuous pilot-plant-scale process for the production of a pure, high-surface-area tungsten metal powder. Ammonium paratungstate

TABLE VII

Organizations Capable of Supplying Sub-Micron Tungsten Metal Powder on a Commercial Basis

Organization	Average Particle Size	Particle Size Distribution Range
General Electric Company	.8 to 1.0 micron	--
Reduction & Refining Co.	.1 to 1.0 micron	--
Shieldalloy Corporation	.4 micron	.05 to 1.5 micron
Sylvania Electric Products	.02 to 1.0 micron	Varies, can be supplied with powder above .5 micron
Union Carbide Metals Co.	.02 micron	.01 to .05 micron
Vitro Laboratories	.02 to .5 micron	.01 to 1.0 micron

is utilized in the process as feed material. Particle size is controlled by the precipitation of tungstic acid from the ammonium paratungstate solution with nitric acid in a jet-type precipitator. The tungstic acid is calcined to a high-surface-area tungsten trioxide and passed through an inclined rotary kiln at moderate temperature (550°C.) while in contact with flowing dry air. This operation decreases the carbon impurity level through oxidation. The purified tungsten trioxide is then passed through an inclined rotary kiln at high temperature while in contact with a flowing purified hydrogen atmosphere. The product is a pure, high-surface-area, pyrophoric tungsten metal powder with an average particle range of .04 to .10 micron. Figure 8 shows the effect of reduction temperature on surface area.

Lamprey and Ripley[31] describe the process used at Union Carbide Metals Company, Niagara Falls, New York, for producing tungsten and molybdenum metal powder of 0.01 to 0.1 micron average particle size by hydrogen reduction of the metal chlorides. Purified hydrogen and tungsten or molybdenum chloride vapors, carried in a stream of argon or chlorine, are preheated to the chosen temperature and brought together in a large reaction space; the gases react immediately on contact to form sub-micron metal powder and hydrogen chloride vapor. The metal may be collected by gravity settling, with or without the use of an electrostatic precipitator; or the reaction gases may be filtered through a large diameter column of steel wool, the trapped powder shaken free of the wool and separated from small steel fragments by magnetic means. The authors point out that, while the overall process works well for producing sub-micron powder down to 0.01 micron particle size, various chemical and mechanical refinements are necessary to the process in order to control particle sizes within narrow ranges, to operate with high materials efficiency and to produce powder of high purity. Table VIII gives some of the reactant data developed from the process.

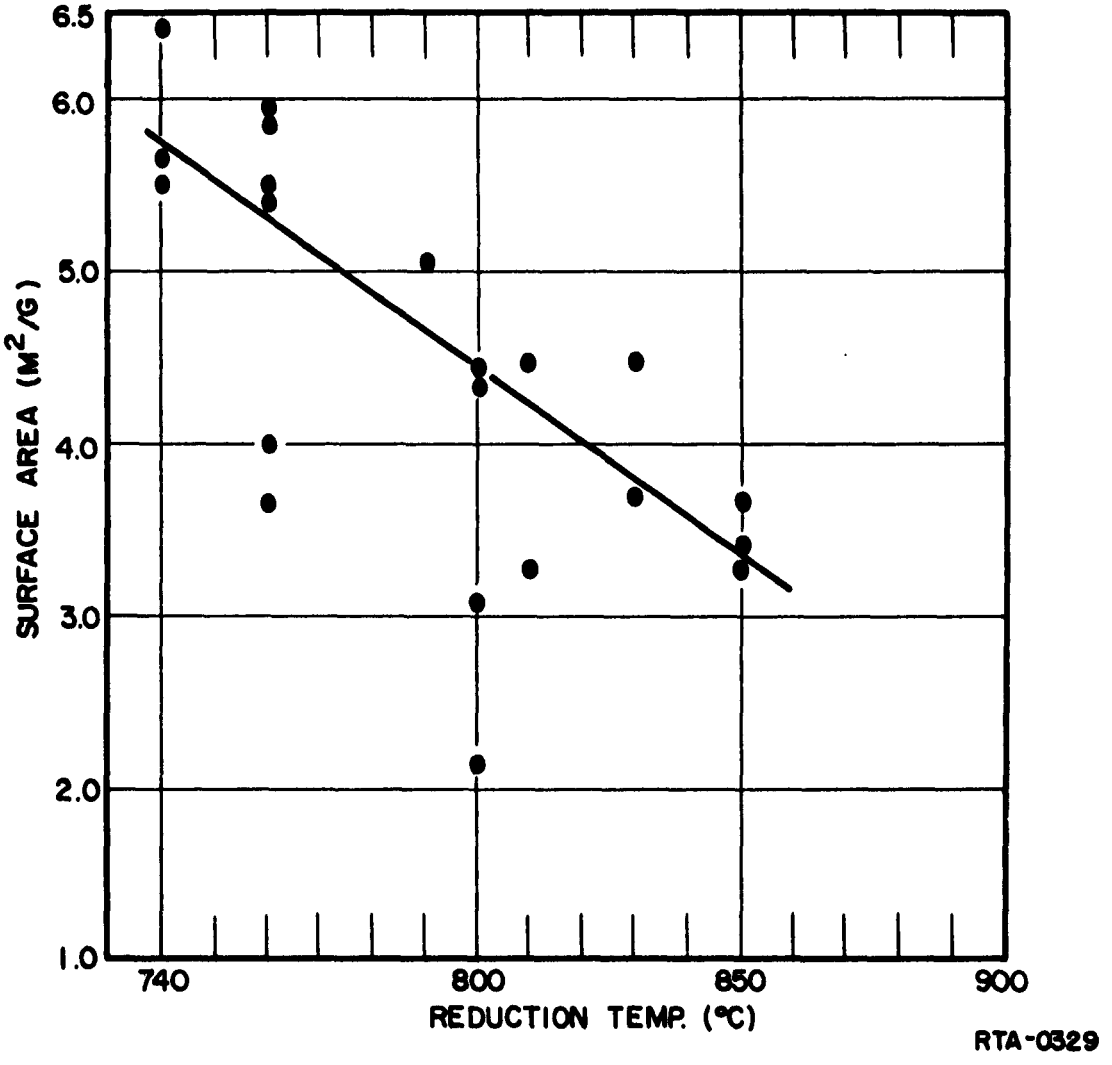

FIGURE 8
EFFECT OF REDUCTION TEMPERATURE ON SURFACE AREA

TABLE VIII[31]

Production of Ultra-Fine Tungsten Powder By The Hydrogen Reduction of Tungsten Hexachloride at Various Temperatures

Run No.	Preheat and Reaction Chamber Temperature, °C.	% Chlorine In Product	Product Diameter In Microns
1	430	1.82	0.029
2	620	.24	0.025
3	695	.10	0.031
4	800	.27	0.026
5	905	.13	0.021

Sylvania Electric Products, Towanda, Pennsylvania, have reported a proprietary method of producing sub-micron size tungsten metal powder by the hydrogen reduction of fine tungsten trioxide. The particle size produced can be controlled from .02 to 1.0 microns.

G. Brauer[32] has made investigations into the reduction of WO_3 from ammonium paratungstate, with zinc powder. The reduction is carried out at 800-900°C. for one hour or 600°C. for two hours. After cooling, the sintered and partly melted product was treated with HCl. The resultant sedimentation of tungsten particle produced a particle size of .05 to 0.1 micron.

Vitro Laboratories[33], under Air Force Contract Number AF 33(600)-42916, has developed a method for the production of sub-micron tungsten metal powder utilizing the Hierarc Process. This process features a high-intensity type electric arc as the energy source. The process material is incorporated into the anode and vaporized by the action of the arc. The particulation results from the condensation of super-cooled effluent vapors. The process has been used to produce sub-micron powders of various oxides, metals,

carbides, etc. and various modifications of the process have been developed in order to adapt the process to materials of different physical properties. In the development of sub-micron tungsten metal powder, it was found that the most effective method was the formation of a sub-micron tungsten oxide by the arc vaporization process and subsequent reduction of the oxide by hydrogen. In preparing the tungsten oxide, homogeneous, low carbon tungsten oxide electrodes were subjected to a variety of processing conditions. A summary of the tungsten oxide arc tests is presented in Table IX.

The improvement in the product for the triple cathode tests 7 and 9 (carbon reduced from 0.15 to 0.07 wt.% and surface area increased from 14.5 to 37.5 m^2/gm) is attributed to the increase quench rate used for this test. As noted in Table IX, the jet quench medium was oxygen. In the first triple anode test, the flow rate was 3 CFM and in the second test it was increased to 10 CFM.

The hydrogen reduction of the resulting oxide was carried out under batch conditions using a fixed charge of powder and a moving gas stream. Various powder charging arrangements were investigated in order to produce a high surface area, high purity metal. The most effective was a multiple shallow tray arrangement and a series of tests were carried out to achieve optimum reduction conditions. A summary of typical reduction conditions and some product characteristics for the tests completed is presented in Table X.

The data illustrates the dependency of the product purity and size on the time-temperature conditions of reduction. High surface area products were generally prepared by reducing the oxide at lower temperatures for extended time periods. Decreasing the time and/or increasing the temperature resulted in lower surface area products. Product purity (tungsten metal content) appeared to be directly

TABLE IX

Tungsten Oxide Arc Tests[25]

Test No.	Carbon in Electrode Wt.%	Cathode Geometry	Arc Power KW	Quench Conditions CFM		Product Carbon Wt.%	Product Surface Area m^2/gm
				Air	Oxygen		
4	2.6	1 @ 55°	8	--	--	0.15	14.2
5	5.3	1 @ 55°	8	--	--	0.31	--
6	5.0	1 @ 55°	11	0.5(1)	--	0.29	--
7	5.0	3 @ 90°	18	0.5(1)	3.0(2)	0.15	14.5
9	5.0	3 @ 90°	6	0.6(1)	10.0(2)	0.07	37.5

(1) Hollow Electrode Injection

(2) Quench Jet Injection

TABLE X

Tungsten-Hydrogen Reduction Tests

	Test No.	Reduction Conditions	Product Analysis Carbon Wt.%	Tungsten Wt.%	Surface Area m2/gm
A.	Six Hour Reduction Series				
	W-9	Max. 825°C., Soak 825°C. 20 minutes	0.050	99.8	6.6
	W-10	Max. 850°C., No Soak		99.6	10.0
	W-15	Max. 800°C., Soak 800°C. 2 hours		99.9	4.7
B.	Twenty-four Hour Reduction Series				
	W-29	Max. 600°C., Soak 600°C. 1 hour	0.062	98.8	30.3
	W-30	Max. 600°C., Soak 600°C. 2 hours	0.14	97.5	31.5
	W-31	Max. 700°C., No Soak		98.6	12.1
C.	Nineteen Hour Reduction Series				
	W-34	Max. 620°C., No Soak		99.1	29.1
	W-36	Max. 620°C., Soak 620°C. 2 hours		99.3	29.0
	W-42	Max. 700°C., Soak 700°C. 2 hours	0.09	99.4	21.6

related to temperature. The higher the final reduction temperature, the higher the metal purity. The optimum conditions were judged to be the nineteen hour reduction series with final temperatures in the order of 620-700°C. (tests W-36 and W-42). These products had surface areas of 21.6 to 29.0 m^2/gm and a tungsten metal content of 99.3-99.4 wt.%. An electron micrograph of the sub-micron tungsten produced by the Hierarc Process is shown in Figure 9[33]. (Note the wide distribution and high agglomeration tendencies typical of this type powder.)

The almost universally accepted method of measuring the particle size of the ultra-fine tungsten powder is by the BET method. This method measures the total exposed surface area of the particles by the absorption of an inert gas by the powder. If the surface area is known, the diameter can be calculated from the relation:

$$SA = \frac{6}{\rho \cdot x}$$

where: SA is the surface area in square meters per gram of material;

ρ is the density of the particle; and

x is the mean particle diameter in microns.

The method assumes a spherical shapes of the particles, but it is estimated in practice, that the deviation rarely exceeds a 5% error.

Particle size distribution measurements have not been determined on this particle size range due to the inadequacy of existing equipment. All organizations actively working with the powders rely on electron micrographs for visual observations or comparisons or to actually measure the particles and estimate the distribution curve.

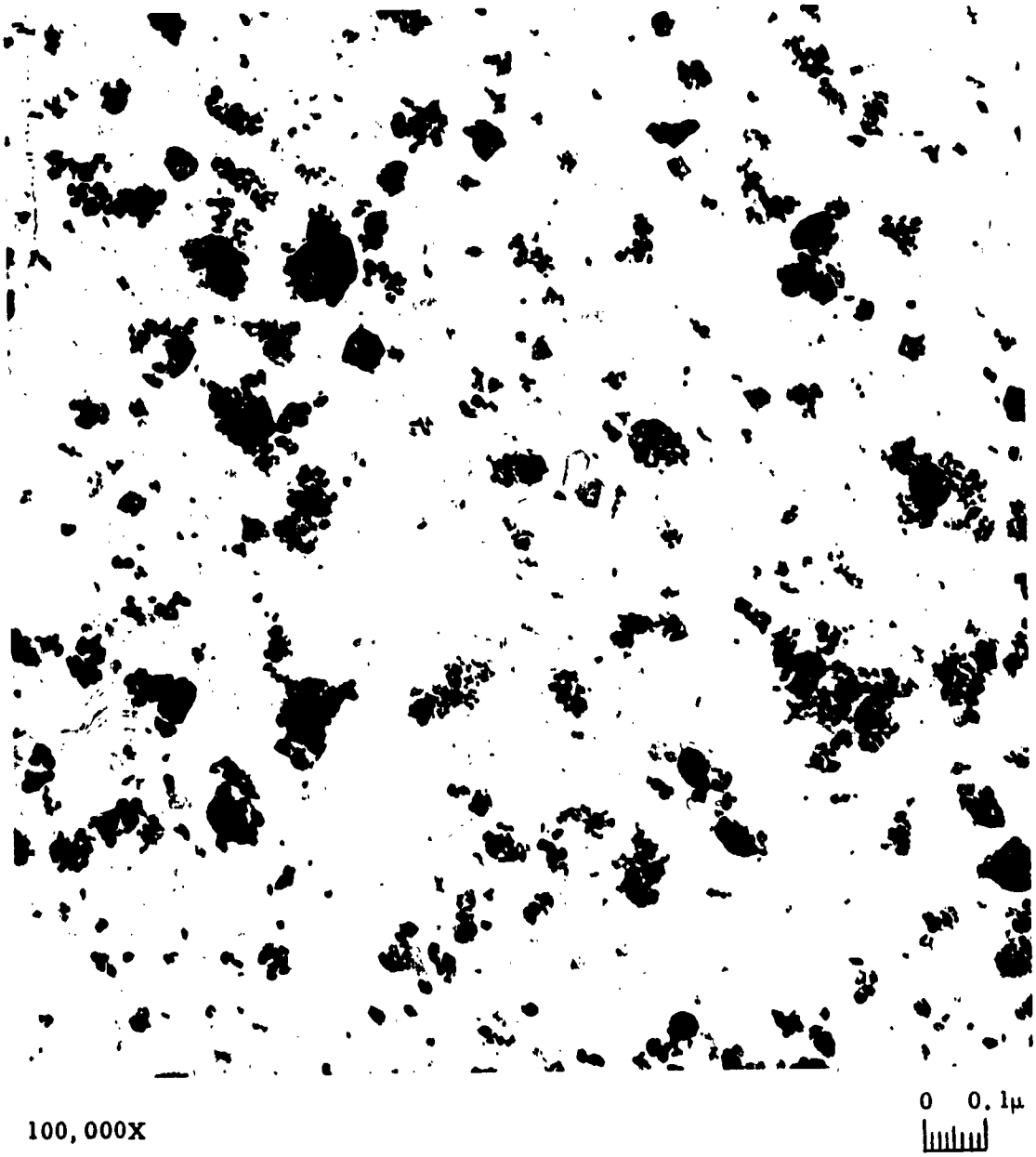

FIGURE 9
ELECTRON MICROGRAPH OF SUBMICRON TUNGSTEN

3. Purity

In the development work on ultra-fine tungsten powders, the object has been to attain the highest degree of purity coupled with the retention of the ultra-fine particle size. The various processes that have been described tend to generate impurities indicative of the particular process used. In general, the metallic impurities (although not reported by the producers) would remain at the same relative levels as standard powders. However, in dealing with the high surface area of the ultra-fines, the reduction process is more difficult and the reduced powder is highly susceptible to atmospheric contamination. Table XI lists the average impurity levels of the ultra-fine tungsten powders from various organizations.

In the processing of standard tungsten powders, the oxygen content can be reduced to substantially low levels in the pre-sintering and sintering operations. Low levels of impurity can be attained with high temperature sintering cycles.

Similarly, the ultra-fine tungsten powders will be purified by the sintering operation, but there has been very little work accomplished in this area.

Lambdin and Perry[30] have made a relatively thorough study of the impurity levels associated with high surface area tungsten powders. Table XII gives average metallic impurities of the sub-micron tungsten metal powder.

It was found that the total impurity level of the reduced powder remained about the same as that of the tungsten trioxide feed. Figure 10 is a graph showing the average oxygen content of the powder of a run plotted with respect to the average surface area of the powder. The top line, represented by solid dots, is for powder which was slowly opened to air before sampling, while the lower line, represented by open squares, is for powder which was handled in

TABLE XI

Average Impurity Levels of Ultra-Fine Tungsten Powder From Various Organizations

Organization	Particle Size Range	Average Level of Impurity Wt. % C	O_2	N_2	Cl_2	Other
*Sylvania Electric	.015 - .06	.005	1.0	--	--	<50 PPM each
	.06 - .1	.005	0.3	--	--	metallic
*Union Carbide Metals	.025 micron	0.1	0.3	--	1500	Si-.05 Total metallic .01-.1
*Vitro Laboratories	.01 micron	.09	2.0%	.075	--	--
Union Carbide Nuclear (Oak Ridge)	.04 - .1 micron	.005	<1.0%	.045	--	--
Bureau of Mines, Albany Metallurgy Research Center	.02 - .04 micron	.01	1.0%	.002	--	--

* - These organizations are supplying or can supply commercial quantities of ultra-fine tungsten metal powder.

TABLE XII

Average Impurities in Tungsten Metal Powder

Run	Average Total Impurity (PPM)	Average Level (PPM)					
		Carbon	Copper	Iron	Silicon	Chromium	Other
47	108	73	3	18	3	5	6
48	62	50	4	0	0	3	5
49	165	52	23	44	4	10	32

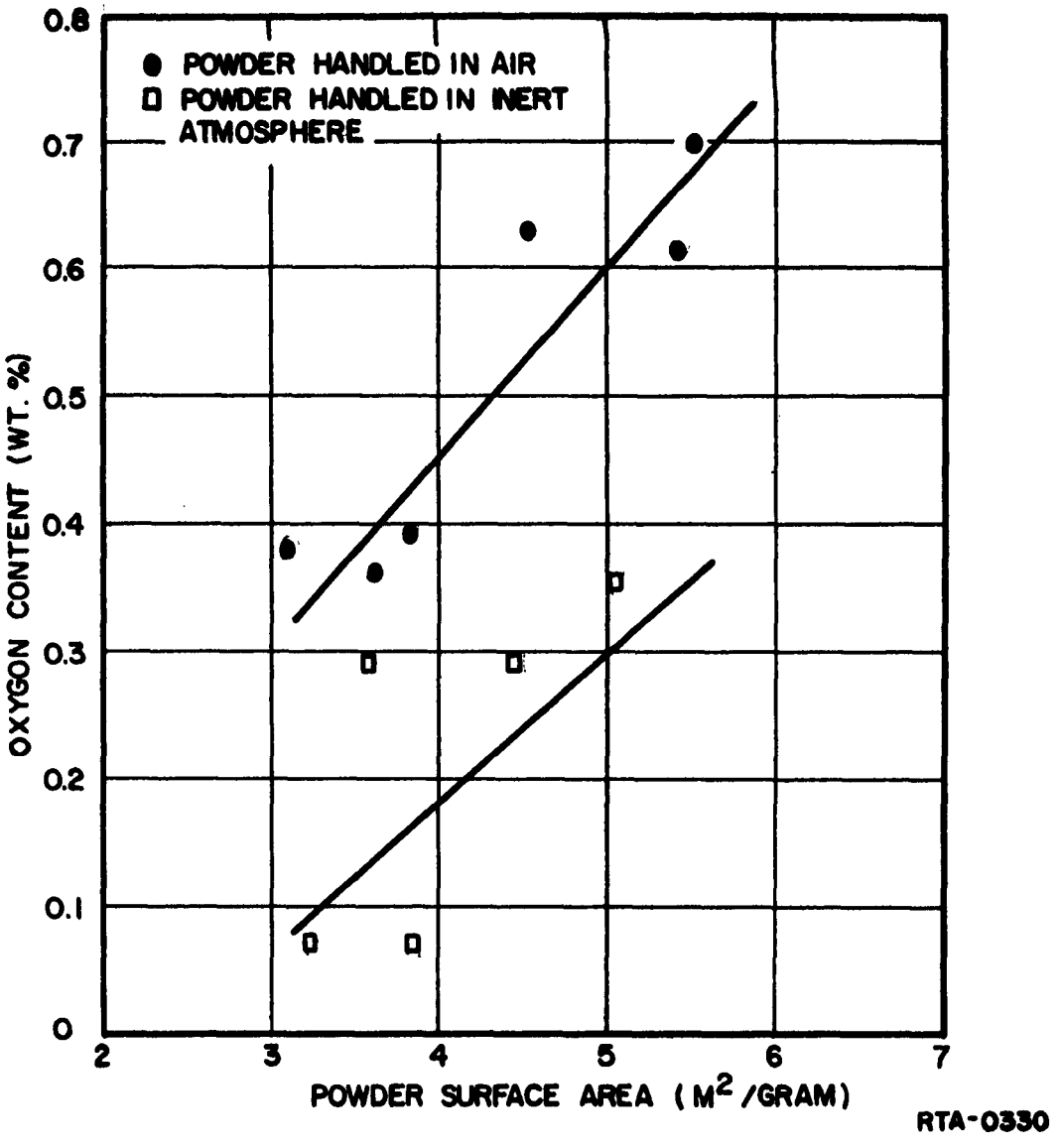

FIGURE 10

EFFECT OF SURFACE AREA ON THE OXYGEN CONTENT OF TUNGSTEN POWDER

an inert atmosphere box. Figure 11 is a graph showing the relationship between nitrogen and oxygen in high-surface-area tungsten powder. The graph shows that as the oxygen content of the high-surface-area powder is reduced (probably below the equilibrium level which would be established if exposed to air) the nitrogen content increases very rapidly. Since there is no apparent correlation between powder surface area and nitrogen content, the increase in nitrogen content is considered to be due to the reactive nature of the powder not in equilibrium with oxygen. Nitrogen levels of about 100 PPM are shown to be normal in powders which have an oxygen content of 0.7 wt.% or above.

Analysis of pressed and sintered test pellets from this powder showed the following average results:

Oxygen - 20 PPM
Carbon - 20 PPM
Nitrogen - 30 PPM

This data indicates that the nitrogen concentration and other interstitial contaminants of the tungsten powder is lowered drastically by the hydrogen sintering process. However, results of tests run on plugs having higher oxygen contents show that density is retarded in the sintering operation.

Union Carbide Metals Company have reduced the oxygen content on sintering from .3% to .05%. This has been on only initial investigations.

The survey indicated that purity determinations were taken from samples that were kept under inert atmosphere at all times. When transfer to the appropriate chemical apparatus was necessary, a known weight of powder was placed in a tin shell, also of a known weight, and the tin shell was crimped on all sides before being transferred to the apparatus (oxygen and nitrogen determinations.) Another method used by NASA was to keep the powder product under organic solvents.

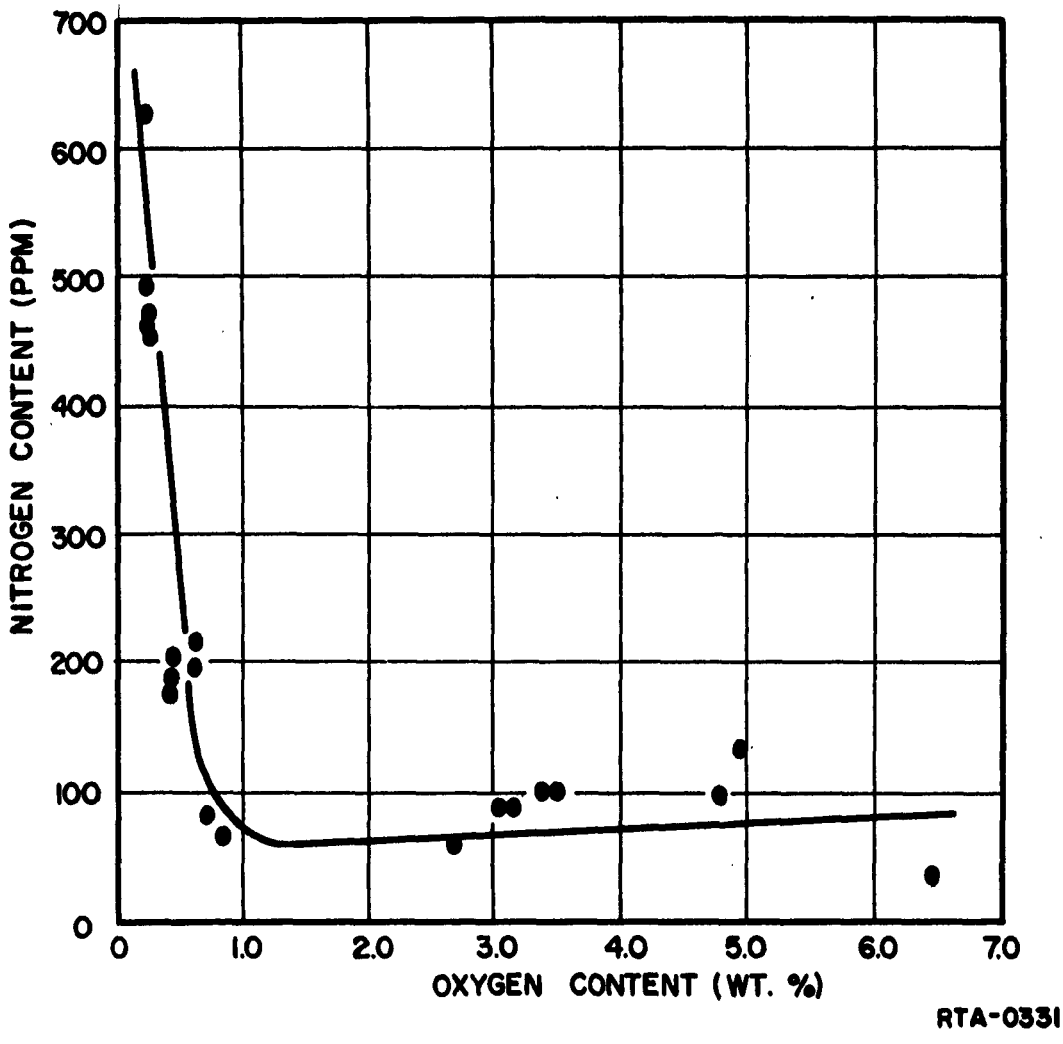

FIGURE 11

RELATIONSHIP OF NITROGEN AND OXYGEN LEVELS IN HIGH-SURFACE-AREA TUNGSTEN POWDER

The method used by various organizations to determine interstitial and metallic chemistry of the ultra-fine powders is shown in Table XIII.

TABLE XIII

Chemical Methods Used By Various Organizations
To Determine Interstitial and Metallic Impurities

	Methods			
Organization	Carbon	Oxygen	Nitrogen	Metallics
Sylvania Electric	Leco Conductimetric	Inert Gas Fusion Vacuum Fusion	Micro-Kjeldahl Vacuum Fusion	Spectrographic
Union Carbide Metals	Leco Conductimetric	Vacuum Fusion	Vacuum Fusion	Emission Spectrograph Mo & Cl Wet Chemistry
Vitro Laboratories	Leco Conductimetric	Vacuum Fusion	Micro Kjeldahl	Spectrographic
Union Carbide Nuclear (Oak Ridge)	Leco Conductimetric	Leco Conductimetric	Micro Kjeldahl	Spectrographic

4. Handling

The survey results indicate that all commercial suppliers of sub-micron size tungsten powder keep the powder under inert atmosphere (usually argon) at all times, whether in process or in storage. This is accomplished by the use of dry boxes, under inert atmosphere, and containing entry ports with rubber gloves attached, to allow for handling powder for compaction, sampling, storage, etc. The powder is usually packed for storage by placing in glass jars with tight sealing rings and/or sealing the lid with paraffin or other suitable sealers. For more massive storage, plastic

bags are loaded and sealed under argon or dry nitrogen and placed in metal cans which are flushed with argon or dry nitrogen and tightly sealed.

Most producers of standard tungsten powders also use inert atmosphere for storage or shipment of their finer grades. Information from these sources indicate that there is no appreciable oxygen pickup, when stored in this manner, over a three-month period; however, no data was obtained on this point.

With respect to the ultra-fine powder, the oxygen pickup in storage has not been very thoroughly investigated. The Bureau of Mines, Albany Metallurgy Research Center, has reported a .4% oxygen pickup per day on .03 micron powder, stored under argon, to a maximum of 5% oxygen content. Sylvania Electric Products, Inc. report that oxygen pickup in storage is very slow with powder above .06 micron particle size when properly stored.

A typical method of powder handling in process is described by Lambdin and Perry[30] in their work on high surface area tungsten powder. The product tungsten powder was collected from the rotary kiln reduction operation by the use of a Pyrex cylinder through a double-ball-valve arrangement. A flange connection between the ball valves permitted the changing of cylinders. A small purge valve connected to the product cylinder permitted inert gas purging and evacuation of an empty cylinder. The filled product cylinder was attached to the inert atmosphere box for removal of powder. This attachment was through a flanged flexible steel hose and double-ball-valve arrangement. The section between the ball valves could be evacuated and purged with inert gas. Product cylinders were allowed to fill with powder before they were removed from the kiln. The tungsten powder was sampled, packaged or compacted for pressing in the inert atmosphere box.

5. Safety Factors

In considering sub-micron powders from a safety standpoint, there are two basic hazards to consider:

1. Rapid oxidation of the powder when exposed to air.
2. Inhaling of powder suspended in air.

Almost all metals combine easily with the oxygen of the air and give off heat when they do. Clean, unoxidized sub-micron powders have a very large surface on which the oxidation reaction can take place. Consequently, the process of oxidizing the powder can take place in a very short time, giving off all the heat at once. This can happen when settled powder is suddenly exposed to air, in which a rapid burning effect will result. However, if the powder is agitated in the presence of air, such as spilling, breakage, etc., and a dust cloud forms, the burning can be so fast and violent as to result in an explosion.

Very little is known of the effect of sub-micron powders on the human body but they are believed to be potentially dangerous, especially when inhaled. Also, skin irritations in the form of severe rashes have been caused by fine powders in contact with the skin.

NASA, in their work with sub-micron powders, have outlined safety regulations for handling the powders, the most important areas covered were as follows:

a. All sub-micton powders should be labeled with a distinctive emblem.

b. All containers, either as-received or for storage, should be marked with this emblem.

c. Only authorized personnel should hanfle the powders.

d. The preferred and approved storage container is a gas-tight metal "reuseable container" can fitted with rubber gasket and clamping ring. Inside the can, under argon,

should be a double plastic bag containing the powder, also under argon. The outer plastic bag should be heat sealed.

e. Use of glass jars should be discontinued.

f. Powder storage containers should be opened only in argon-filled glove boxes by authorized persons.

g. Opening of shipping drums should be done with extreme care due to the possibility of a damaged storage container releasing loose powder inside the drum.

h. Drums should be opened by authorized persons wearing safety goggles with side shields, air-line respirators and fire retardent clothing. A dry powder-type fire extinguisher should be on hand.

i. Arrange work so as to uncover no more than five pounds (2,270 grams) of loose powder inside box at any time.

Lamprey and Ripley[31] have found that there is great variability in the reactivity of tungsten powder toward air. Some samples oxidize rapidly on exposure to air. For example, when a sample containing 1.5% of absorbed chlorine was exposed to air at room temperature, the powder showed temperature rises of 10-20°C. due to air reaction, but no ignition occurred. Other samples, exposed to air, have become red hot on the surface within a few seconds' time. Factors such as the rate of heat loss from the powder and the degree of packing of the sample also effect the possibility of ignition.

These tests indicate that the fine tungsten powder can be handled safely if a few simple precautions are taken. However, any finely divided metal powder, mixed with air or other oxidizing agent, is a potential source of uncontrollable reactions.

6. Compaction

The experience on compaction of the ultra-fine powders, according to survey visits, have been varied. This is possibly explained by the fact that the physical and chemical characteristics of the powders are considerably different. Because of the low bulk density of the ultra-fine powder in comparison to standard size powders, the "as pressed" density is much lower. Entrapped air or gas, friction due to high surface area, and the light, fluffy nature of the powder on initial fill are considered prime causes for the lower "as pressed" densities. The bulk density of some of the powders produced by various organizations and their effect on pressed density are given in Table XIV.

TABLE XIV

Organization	Bulk Density (% of Theo.)	Pack Density (% of Theo.)	Pressed Density (% of Theo.)
Sylvania Electric	10% to 13%	--	--
Union Carbide Metals	1.0%	9% to 15%	50%
Vitro Laboratories	2.9%	--	--
Union Carbide Nuclear (Y-12 Oak Ridge)	3% to 13%	5.7% to 19%	36%

A standard Scott Density technique is used by most producers to determine bulk density. Vibratory means have been utilized to increase the pack density of the material so that a more uniform size final pressing can be attained.

A few producers have found that a prepressing operation at low pressures (1000-5000 psi) to agglomerate the particles prior to final pressing is helpful. The powder is crushed between pressing operations and this increases the bulk density and gives a higher pressed density and better control of pressed shape. It has been the experience of at

least one producer that single stage pressing is unsuccessful. All pressing that has been done to date on ultra-fine powders has been done using isostatic pressing procedures. Lambdin and Perry[30] have plotted prepressed and single pressed powders with respect to green density versus surface area (Figure 12). The upper curve is plotted from pellets which were isostatically pressed at 30,000 psi, broken up to pass a 35 mesh screen and then pressed again in the same manner. The graph shows, generaly, that the green density can be increased approximately 4% at any surface area by prepressing under the conditions described.

7. Sintering

There is very limited information available on the sintering parameters of ultra-fine tungsten powder. The most complete investigation has been carried out by Lambdin and Perry[30] where they record the effect of surface area on sintered density and the effect of temperature and time on sintered density.

Table XV gives data generated from four powders with varying surface areas and varying oxygen content when sintered at 1500°C. for three (3) hours. The increased density was accompanied by increased grain growth, which is to be expected due to the proven fact that grain growth is accelerated during sintering with finer initial grain size.

Table XVI gives data generated from one powder source and two different sintering cycles. Again, the higher temperature, longer time sintering cycle resulted in a higher sintered density and larger grain structure.

Lamprey and Ripley[31] made a few preliminary sintering tests on the powder they had developed (.02 micron) in order to observe sintering characteristics. Specimens of rather impure powder (0.6% oxygen and 0.3% chlorine) were pressed at 40 tons per square inch giving compacts of 40%

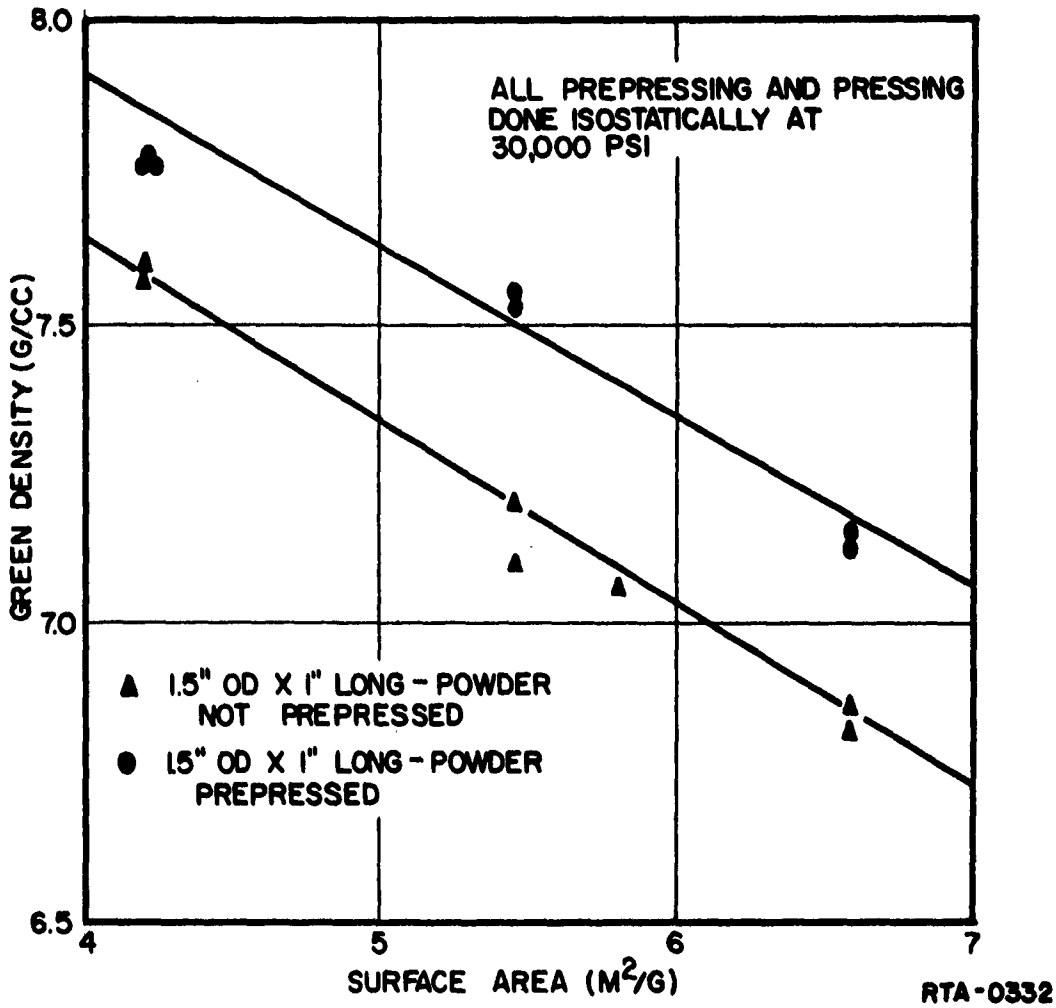

FIGURE 12

GREEN DENSITY OF PRESSED TUNGSTEN PELLETS

TABLE XV[22]

Sintering Data From Four Ultra-Fine Tungsten Powders With Varying Particle Size

	Powder			
	A	B	C	D
Metal Powder				
Reduction Run Number	17	19	19	Batch
Batch Number	6	7	1	Reduced
Surface Area (M^2/g)	2.61(.12)	3.09(.10)	4.68(.067)	10.12(.03)
Oxygen (%)	.326	.352	.463	1.70
Reduction Temp. (°C.)	800	850	850	700
Compacting (Isostatically)				
Pressing Pressure (PSI)	30,000	30,000	30,000	30,000
Green Pellet Size (Inch OD)	0.5	0.5	0.5	0.5
Green Pellet Density (g/CC)	8.14	7.37	7.69	--
Sintering				
Atmosphere	Hydrogen	Hydrogen	Hydrogen	Hydrogen
Temperature (°C.)	1500	1500	1500	1500
Time (Hours)	3	3	3	3
Measurements				
Sintered Density (g/CC)	16.99	17.18	18.21	18.14
Theoretical Density (%)	88.03	89.02	94.35	95.00

TABLE XVI

Sintering Data From One Ultra-Fine Powder Source At Two Different Sintering Cycles

	Powder A	Powder B
Metal Powder		
Reduction Run Number	18	18
Batch Number	19	19
Surface Area (M^2/g)	7.57(.042)	7.55(.042)
Oxygen (%)	1.20	1.20
Reduction Temperature (°C.)	800	800
Compacting (Isostatically)		
Pressing Pressure (PSI)	30,000	30,000
Green Pellet Size (Inch OD)	0.5	1.5
Green Pellet Density (g/CC)	8.87	7.14
Sintering		
Atmosphere	Hydrogen	Hydrogen
Temperature (°C.)	1700	1850
Time (Hours)	1	8
Measurements		
Sintered Density (g/CC)	17.23	18.44
Theoretical Density (%)	89.27	95.54

theoretical density with good green strength. These specimens sintered poorly at 1750°C. giving compacts of 80% theoretical density. However, grain growth at this temperature was excessive, approaching approximately 30 microns. Similar compacts were then sintered 1550°C. for 30 minutes in hydrogen atmosphere to give products of 94% theoretical density.

Mundinger, Hausner and Leng[34], in a study of the pressing and sintering behavior of mixtures of conventional and ultra-fine tungsten powders, added 3.7 square meters/gram surface area tungsten powder (.082 micron), in amounts up to 25%, to commercial tungsten powders of 2, 4.5, and 6.8 micron average particle size. Table XVII gives the results of these additions on the final pressed and sintered density. The material was compacted at 60 tsi pressure and sintered at 1700°C. for three hours in hydrogen. Figure 13 gives a visual representation of these data. The densities of the pressed compacts varied from 69% of theoretical for the 2 micron admixture to 76% for the 6.8 micron admixture. Upon sintering, the corresponding values were 92% and 80%. The highest sintered densities were obtained in all cases with the largest addition of ultra-fine powder.

8. Conversion Practice

There is only token data available on conversion experience with respect to ultra-fine powder. Union Carbide Nuclear, in the Y-12 Facility, Oak Ridge, Tennessee, have made initial attempts to roll sintered compacts approximately 1" x 4" x 4" that were processed from ultra-fine powder. In general, their findings indicated that higher temperatures and smaller reductions were necessary as compared to the rolling characteristics of conventional powder. Grain boundary fracture was encountered when rolling at 1700°C.

TABLE XVII

Effects of Composition on the Compacted and Sintered Density of Mixtures of Ultra-Fine Tungsten With Commercial Grade Tungsten Powder of Three Particle Sizes

Specimen Number	Composition		Density, % Of Theoretical		Density Increase During Sintering
	Commercial W Size(In Microns)	Ultra-Fine W % Addition	As-Pressed (dp)*	As-Sintered (dp)**	ds-dp
1	2.0	0	68.6	87.1	18.5
2	2.0	15	68.7	87.2	18.5
3	2.0	25	69.3	92.4	23.1
4	4.5	--	71.9	77.2	5.3
5	4.5	15	73.2	81.0	7.8
6	4.5	25	72.6	86.6	14.0
7	6.8	--	73.0	74.4	1.4
8	6.8	10	76.1	79.6	3.5
9	6.8	15	75.6	80.7	5.1
10	6.8	25	72.8	82.7	9.9

* - Pressing pressure, 60 TSI
** - Sintered at 1700°C. for 3 hours in H_2

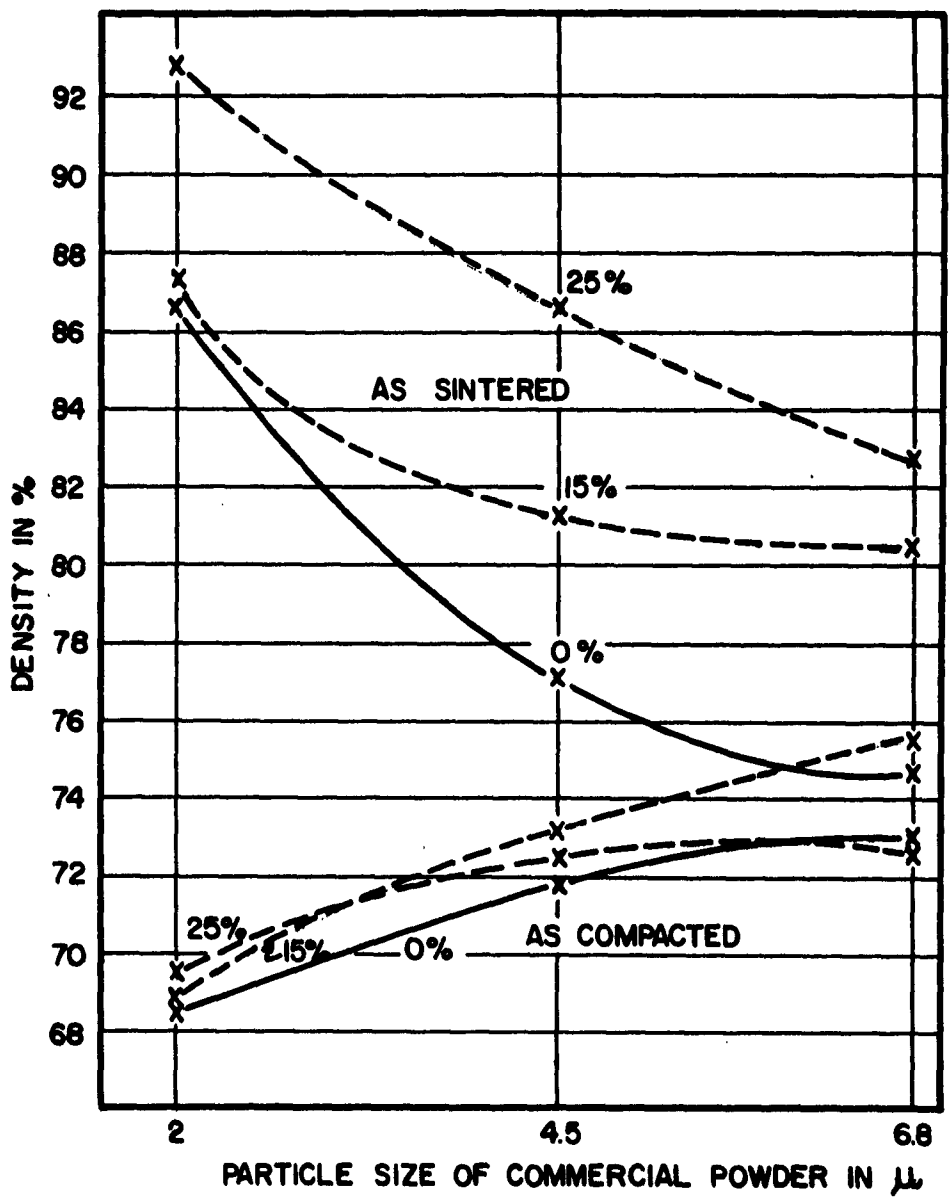

FIGURE 13

DENSITIES OF COMPACTED AND SINTERED TUNGSTEN POWDERS OF 2, 4.5 AND 6.8 MICRON PARTICLE SIZE, WITH AND WITHOUT ADDITION OF 15 AND 25% ULTRA-FINE TUNGSTEN POWDER

Reducing .530" gauge to .453" was accomplished in three passes at 1740°C./1850°C. before the material cracked on the fourth pass at 22% total reduction. Material with 88-89% density broke up when rolled at 1450°C. (on first pass).

9. Summary

From the survey results, there are approximately seven organizations that have produced sub-micron size tungsten metal powder. Of these, only three organizations are prepared to offer commercial quantities of powder for sale. The market demand for powder of this type has not developed other than for some applications of direct sintering of massive tungsten shapes to a high density final product. As a result, the technology of the material is not very far advanced.

The commercial suppliers have produced sub-micron powder from a variety of processes including the following:

a. Direct hydrogen reduction of ultra-fine tungsten oxide which is prepared by a proprietary process.

b. Direct hydrogen reduction of ultra-fine tungsten hexachloride.

c. Direct hydrogen reduction of ultra-fine WO_3 prepared by the arc vaporization technique (Hierarc Process).

The total impurity levels and the specific impurities vary considerably between processes but, due to the high surface area generated by each process, the major impurity is oxygen. The overall oxygen content of the powders range from 0.05 to 1.0% depending upon total surface area.

All suppliers use inert atmosphere for handling and storage. The powder is mildly pyrophoric in the range of 0.1 to 1.0 micron and violently pyrophoric in the range of .1 micron and smaller. Care in handling is highly emphasized.

Physical characteristics of the powders also vary with the reduction techniques. Bulk densities of 1 to 10% have been reported. Average grain size ranges from .015 to 0.1 microns as calculated from surface area measurements using the B.E.T. gas absorption method. Particle size distribution is not measured directly due to equipment limitations. The particle size distribution is estimated from photographs of the powder taken by electron transmission microscopy.

Compacting is usually accomplished by isostatic pressing where pressed densities of 40-50% of theoretical are attained. In some cases double pressing procedures are used to increase green strength.

Only limited and widely diversified data are available on consolidation and purification during sintering. In general, the sintered compacts exhibit high density and abnormal grain growth at high sintering temperatures. The oxygen, nitrogen and carbon contents are lowered with sintering cycles involving higher temperatures and long hold times. However, this type of sintering cycle is usually detrimental to further fabrication. Sintering cycles involving low temperatures and short hold times, lessen grain growth and increase fabricability, if high enough densities can be attained.

There is very little data available on the fabrication of sintered shapes, made from sub-micron size tungsten powder, to final sheet product. However, optimum rolling parameters for tungsten sheet have been developed on two government contracts.

The addition of either ThO_2, ThO_2-Na_2O or ZrO_2 in the form of fine dispersoid particles to conventional tungsten powder, resulted in grain growth inhibition and had a marked effect in lowering the ductile to brittle transition temperature of wrought and recrystallized tungsten. Also, prior grain size has been shown to affect the transition temperature of wrought tungsten, with finer grain size tending to lower the transition temperature.

III. Future Work - Phase II

A. Recommendations

On the basis of the findings of Phase I, the following recommendations are made:

1. Due to the limited number of commercial producers of ultrafine tungsten powder and the large variation between producers with respect to physical and chemical properties, it is recommended that three commercial powders be initially evaluated for purity, ease of consolidation and fabrication and resultant physical and mechanical properties.

2. Based on the inherent tendency for high-surface-area powders to contain high levels of impurity and to exhibit rapid grain growth on sintering, it is recommended that a two-fold evaluation be considered:

   a. The effect of a high temperature purification sintering cycle on ultimate fabrication and mechanical properties. This treatment would tend to give a high density, large grain size and relatively high purity sintered shape.

   b. The effect of a low temperature sintering cycle on ultimate fabrication and mechanical properties. This treatment would tend to retain the inherent sub-micron grain size with a higher impurity level but a more easily workable sintered shape.

3. Recent work has indicated that fractional additions of the sub-micron powder to conventional powder particle sizes has a marked effect on sintering cycles, final density and final grain size. An investigation of this effect on further fabrication is also recommended.

4. The effect of true hot working in an inert atmosphere and subsequent hot/cold working to finished product should be

demonstrated, through utilization of the InFab Facility and measurement of the physical, chemical and mechanical properties of the sheet.

5. Based on the results of the use of dispersion phases on the recrystallization and transition behavior of tungsten, it is further recommended that consideration be given to a small amount of work in which intentional additions of thoria and/or zirconium oxide be made to sub-micron powder in order to acquire high sintered densities and lower transition temperature.

B. Proposed Program for Phase II

1. Objective

The objective for Phase II work is the evaluation of the physical properties of commercially available tungsten metal powder in the ultra-fine range of particle size and the effect of these physical properties on handling, pressing, sintering and fabrication to sheet product. Also, to establish purity levels and tentative specifications for powder that will be utilized in future work on this program.

2. Powder Procurement

Sub-micron size tungsten metal powder in the average particle size range of .01 to .1 micron will be procured to the suppliers best attainable purity level. Three commercial sources of powder will be obtained for initial pilot evaluation. The powder will be shipped under protective atmosphere as agreed between purchaser and supplier and unpacked and stored in the InFab Facility* for future processing.

* - InFab is an inert atmosphere mill facility constructed and operated by Universal-Cyclops Steel Corporation for the Department of the Navy, Bureau of Naval Weapons under Contract Number NOa 55-006-c.

3. Powder Evaluation

Powder samples will be taken in InFab for the following determinations:

a. Complete Chemistry
b. Particle Size Determination (Surface Area)
c. Particle Size Distribution (Electron Microscopy)
d. Bulk Density

4. Pilot Sample Processing

In order to acquire as much information as possible based on the current State-of-the-Art, the following outline for pilot sample processing is proposed:

a. Supplier "A" - as-received powder
b. Supplier "B" - as-received powder
c. Supplier "C" - as-received powder
d. 10% Supplier "C" powder + 90% commercial powder
e. 30% Supplier "C" powder + 70% commercial powder
f. 50% Supplier "C" powder + 50% commercial powder
g. Supplier "A" + 1% ThO_2 additions
h. Supplier "B" + 1% ZrO_2 additions

It is recognized that the powders from the three suppliers will vary in properties but the results of the additions to the respective powders can be compared to the results of the "as-received" powder and evaluated for the possibility of future work.

5. Pressing

Three samples of each of the eight proposed powder mixes will be loaded in bags in the InFab Facility and isostatically pressed at the best overall pressure for all the mixes. In all, twenty-four (24) sample pressings will be prepared for further evaluation. A constant weight of

powder will be pressed so as to give a sintered size of .750" diameter x .750" high based on a nominal 90% of theoretical density. The respective mixes will be checked for:

a. Bulk Density
b. Tap Density
c. Pressed Density

6. Presintering

The twenty-four (24) pieces will, for simplicity, be presintered at a common time and temperature (1800°F. - eight hours - dry hydrogen atmosphere).

7. Sintering

One sample of each of the eight mixes will be sintered as follows:

a. 2500°F. - four hours - dry hydrogen
b. 3000°F. - four hours - dry hydrogen
c. 3500°F. - four hours - vacuum

The sintered samples will be evaluated for:

a. Final Density
b. Microstructure
c. Hardness

8. Upset Forging

The sintered samples will be ground to uniform size and upset forged by means of a drop weight test using a constant impact energy at a constant temperature that will give reasonable upset values over the range of mixes. The upset tests will be evaluated for:

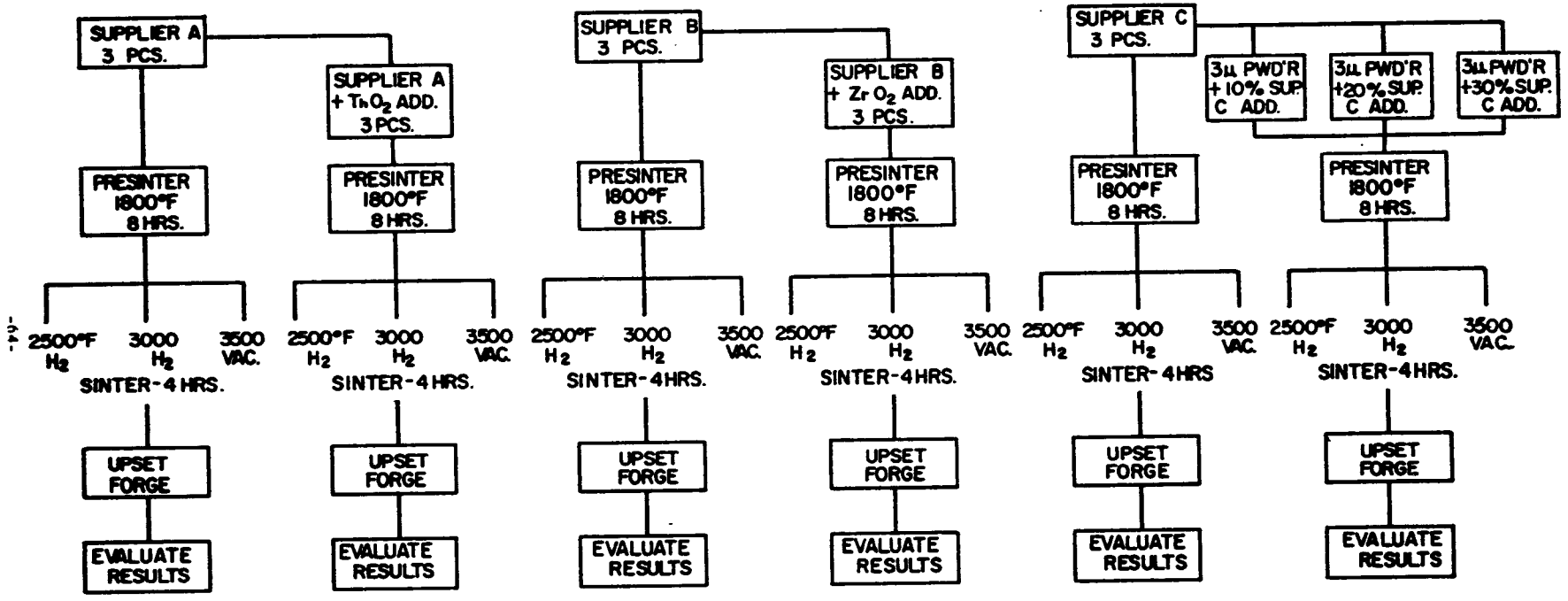

FIGURE 14

PILOT POWDER EVALUATION- PHASE II

RTB-0039

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National Aeronautics and Space
Administration
21000 Brookpark Road
Cleveland 35, Ohio
Attn: Mr. G. Vervin Ault, Assistant
Chief, Materials and Structures
Division, Lewis Research Center

Navy Department
Industrial Planning Division
Attn: E. G. Gleason
Washington 25, D. C.

North American Aviation, Inc.
Attn: Mr. D. H. Mason
Staff Engineering
General Data Section
International Airport
Los Angeles 45, California

North American Aviation, Inc.
Attn: Mr. Jim Huffman
Materials Engineer
International Airport
Los Angeles 45, California

Northrup Corporation
Attn: Mr. R. R. Nolan, Vice President
1001 E. Broadway
Hawthorne, California

Nuclear Metals, Inc.
Attn: Mr. A. Kaufmann
155 Massachusetts Avenue
Cambridge 39, Massachusetts

Pratt & Whitney Aircraft Corporation
CANEL, Connecticut Operations
Attn: Mr. L. M. Raring, Chief
Metallurgical and Chemical Laboratory
P. O. Box 611
Middletown, Connecticut

Reactive Metals, Inc.
Attn: Mr. L. G. McCoy
Government Contract Administrator
Niles, Ohio

Republic Aviation Corporation
Attn: Mr. Adolph Kastelowitz,
Director of Manufacturing Research
Farmingdale, Long Island, New York

Rocketdyne Division
North American Aviation Corporation
Department 574
Attn: Mr. J. D. Hall
6633 Canoga Avenue
Canoga Park, California

Rohr Aircraft Corporation
Attn: Mr. Burt F. Raynes, Vice President
Manufacturing
P. O. Box 878
Chula Vista, California

Ryan Aeronautical Company
Attn: Mr. Lawrence M. Limbach
Vice President, Manufacturing
2701 Harbor Drive
San Diego 12, California

Sandia Corporation
Sandia Base
Attn: Mr. Donald R. Adolphson
Section 1621-1
Albuquerque, New Mexico

Sandia Corporation
P. O. Box 969
Livermore, California

Sikorsky Aircraft Division
United Aircraft Corporation
Attn: Mr. Alex Sperber, Factory
Manager
North Main Street
Stratford, Connecticut

Solar Aircraft Company
Attn: Dr. A. G. Metcalfe,
Assistant Director
Advanced Research
2200 Pacific Highway
San Diego 12, California

Sperry Gyroscope Company
Division of Sperry Rand Corporation
Attn: Mr. F. W. Trunbull
Engineering Librarian
Great Neck, Long Island, New York

Sylvania Electric Products Corporation
Attn: Dr. Paul Pelton
Director of Research
Towanda, Pennsylvania

Sylvania Electric Products Corporation
Attn: Dr. L. L. Seigle, Manager
Metallurgical Laboratory
P. O. Box 59
Bayside, New York

Temco Aircraft Corporation
Attn: Mr. V. N. Ferguson
Manufacturing Manager
P. O. Box 6191
Dallas, Texas

Thiokol Chemical Corporation
Reaction Motor Division
Attn: Mr. W. F. Brown, Manager
Manufacturing Engineering
Contracts Department - Ford Road
Danville, New Jersey

Thiokol Chemical Corporation
Utah Division
Attn: Patrick McAllister
Materials and Processes Section
Brigham City, Utah

Titanium Metals Corporation of America
Attn: Mr. Keith Curry
Toronto, Ohio

Thompson Ramo Wooldridge, Inc.
Attn: Dr. Al Nemy
Engineering Supervisor
23555 Euclid Avenue
Cleveland 17, Ohio

University of California
Radiation Laboratory
Attn: Mr. Duane C. Sewall
P. O. Box 808
Livermore, California

University of California
Los Alamos Scientific Laboratory
P. O. Box 1663
Los Alamos, New Mexico

Wah Chang Corporation
Technical Library
P. O. Box 366
Albany, Oregon

Westinghouse Electric Corporation
Lamp Division
Bloomfield, New Jersey
Attn: Dr. R. H. Atkinson

Westinghouse Laboratories
Churchill Boro
Pittsburgh 35, Pennsylvania
Attn: Dr. J. H. Bechtold,
Manager Metallurgy Department

Wright Air Development Division
Attn: WWRCMP-1
Wright-Patterson Air Force Base, Ohio

Wright Air Development Division
Attn: WWRMES-2
Mr. E. E. Zink
Wright-Patterson Air Force Base, Ohio

Wright Air Development Division
Attn: ASD (ASRCMP-4)
Wright-Patterson Air Force Base, Ohio

Stauffer Metals Company
Attn: Dr. Jack Hum
1201 South 47th Street
Richmond, California

University of California
Lawrence Radiation Laboratory
Technical Information Division
P. O. Box 808
Livermore, California
Attn: Clovis G. Craig

APPENDIX B

Survey Summary

Number of Questionnaires Mailed	236
Total Number of Replies	76
Number Containing Information	32

Companies that have been visited:

Sylvania Electrid Products	Towanda, Pa.
Battelle Memorial Institute	Columbus, Ohio
National Aeronautics and Space Admin.	Cleveland, Ohio
Union Carbide Nuclear Y-12 Facility	Oak Ridge, Tenn.
Union Carbide Metals Company	Niagara Falls, N.Y.
Vitro Labs	West Orange, N.J.

Companies that have been contacted personally:

Reduction and Refining Company	Kenilworth, N.J.
Los Alamos Scientific Laboratory	Los Alamos, N.M.
Union Carbide Nuclear K-25 Facility	Oak Ridge, Tenn.
Monsanto Chemical Company	St. Louis, Mo.
Allied Chemical Corporation	Morristown, N.J.

DEVELOPMENT OF TUNGSTEN SHEET
by the use of
ULTRA-FINE TUNGSTEN METAL POWDER

Contract AF 33(657) - 10513

State-of-the-Art-Survey

Section I - ORGANIZATION

A. Are you a supplier of raw materials for use in producing tungsten?

Yes_____ No_____

A producer of mill shapes?

Yes_____ No_____

A consumer?

Yes_____ No_____

Other Interests: Research_____ Development_____

Other _____

B. Are powder metallurgy techniques utilized to achieve final product?

Yes_____ No_____

C. What form is your starting material and final product?

Starting Material		Finished Product	
a) Ore	_____	a) Para	_____
b) Acid	_____	b) Oxide	_____
c) Para	_____	c) Metal Powder	_____
d) Oxide	_____	d) Sintered Shapes	_____
e) Metal Powder	_____	e) Porgings	_____
f) Sintered Billet	_____	f) Extrusions	_____
g) Porgings	_____	g) Mill forms	_____
h) Extrusions	_____	h) Formed Parts	_____
i) Mill forms	_____	i) Other	_____
j) Other	_____		

D. Do you produce or use tungsten product in the ultra-fine range of particle size (.01-1 micron)?

Yes_____ No_____

SECTION II RAW MATERIAL

A. What maximum levels of impurities of major importance are specified when procuring raw materials of the following forms?

Paratungstate or Oxide		Tungsten Metal Powder		Sintered Shapes		Other
W		W		W		
WO_3		O		O		
NH_3		H		H		
Non Vol. Matter		N		N		
Fe		C		C		
Si		Fe		Fe		
Mo		Si		Si		
Ni		Mo		Mo		
Al		Ni		Ni		
Cu		Al		Al		
Na		Cu		Cu		
Cu		Na		Na		
Other		Ca		Ca		
		Other		Other		

B. What are the powder particle size ranges that are produced or used?

Powder Material	Average Particle Size	Particle Size Range	Particle Size Distribution Range	Particle Shape

C. What alloying and/or "doping" additions, if any, have been investigated.

Element or Compound	Quality Added (or range of addition)	How Added

D. What are the effects of alloying and/or "doping" additions noted in C on grain size, fabricability, and/or properties?

Element or Compound	Quantity Added (or range of addition)	Effect

E. If a producer or user of tungsten metal powder in the ultra-fine range of particle size, do you find it necessary to use protective techniques in sample handling in order to determine chemistry, particle size, particle size distribution, etc. Yes_____ No_____

If "Yes," briefly explain what techniques are used.

F. What method or equipment is used to measure:

Property	Method or Equipment Used	Principle or Theory (Briefly Explain)
a) Surface Area		
b) Average Particle Size		
c) Particle Size Distribution		
d) Apparent Density		

G. What mechanisms are used to acquire a particular particle size range in Tungsten powder?

Particle Size Range	Mechanism Used (H_2 Reduction Ball Melting Etc)	Principle or Theory (Briefly Explain)

H. What is the rate of impurity pick-up experienced in storing Tungsten metal powder?

Particle Size Range	Initial Chemical Determination			Rate of Pick-Up %/day		
	O	N	H_2O(Vapor)	O	N	H_2O(Vapor)

I. In packaging ultra-fine tungsten metal powder for storage or shipment, what protective methods are used?

Method	How Administered (Briefly Explain)
a) Vacuum	
b) Inert Atm.	
c) Other	

Contract AF 33(657) - 10513

SECTION III - CONSOLIDATION

A. Do you compact powder into shapes?

Yes_____ No_____

If answer is "Yes" what methods are used?

Compacting Method	Resulting Shape	Maximum Dimensions of Compacted Shape

B. What powder particle sizes and shapes are required for optimum compacting conditions?

Compacting Method	Average Particle Size	Particle Size Range	Particle Shape

C. What pressing procedures are used?

Pressure	Cold Pressed Density	Lubricant Used (if any)	Die Shape

Additional comments on uniformity of density in cold-pressed shapes:

_____

_____

_____

D. What methods, if any, do you use to increase bulk density prior to compacting?

Method	Equipment	App. Den. Before	App. Den. After

E. What sintering procedures are used?

	Pre-Sinter	Final Sinter
Method of heating (Induction-resist-other)		
Charging method (Stoke-Zone-Direct)		
Temperature		
Time		
Atmosphere		
Resulting as sintered density		

F. What critical chemical reactions, if any, occur on sintering.

G. What average purity levels are obtained in the sintering operations?

Element	Average Analysis On Powder			Average Analysis On Sintered Product		
	Ultra Fine	Fine	Coarse	Ultra Fine	Fine	Coarse
O						
C						
N						
Si						
Mo						
Fe						
Other						

SECTION IV FABRICATION

A. What are the maximum size wrought shapes you have made?

Forgings _____

Extrusions _____

Rolled Bar _____

Sheet:

Gage	Width	Length
<.020		
.020		
.040		
.060		
>.060		

B. What conditions are used in initial breakdown for the production of sheet?

Method of Mechanical Working	Size of Workpiece	Preheating Temperature	Preheating Atmosphere	Lubricant (if any)

Extrusion ratio (if extrusion is used). _____

C. What reduction schedules are used in forging and rolling to sheet?

Working Operation	Preheat Temperature	Amount of Reduction Per Pass	Reduction between Anneals	Annealing Temperature	Annealing Atmosphere

D. What is the size and separating force of your rolling mill?

_____

_____

_____

E. Do you use a protective atmosphere or protective coating?

Yes_____ No_____

Composition of atmosphere or coating, if used.

_____

_____

_____

F. What surface conditioning treatments are used?

	Pickling	Grinding	Other
Intermediate	_____	_____	_____
Final	_____	_____	_____

G. What cutting and/or trimming procedures are used?

	Procedure
Heavy gage (plate)	_____
Light gage	_____
Finish size	_____

H. What flattening procedures are used?

	Procedure
Heavy gage (plate)	_____
Light gage	_____
Finish sheet	_____

What maximum "out of flat" tolerance do you hold? _____

SECTION V TESTING

A. What tensile test Data have you developed on finished product?

Test Condition	Test Temperatury	Strain Rate	Yield Strength	Ultimate Strength

% Elong	% Reduction Area	Elastic Mod	Hardness

B. Creep and/or Stress Rupture Data.

C. Transition Temperature (specify type and testing conditions)

D. Ductility tests (specify type and testing conditions)

E. Recrystallization temperature

Condition of Mat.	Temperature

F. What are your chemical analysis procedures and standards?

For carbon _____

For oxygen _____

For nitrogen _____

For metallics _____ _____

G. What methods are used for inspection of your consolidated product?

Inspection	Method
Density	_____
Cracks	_____
Voids	_____
Other	_____
_____	_____
_____	_____

H. Please discuss any other means of consolidation, etc., not listed above, which you have employed.

_____

_____

I. Additional Comments:

_____

_____

_____

_____

_____

Please attach any data sheets or references to published or internal reports on powder metallurgy Tungsten that are available.

APPENDIX C

Distribution List for Questionnaire

Aerojet-General Corporation
Azusa, California

Aerojet-General Corporation
Downey, California

Aerojet-General Corporation
Solid Rocket Plant
Sacramento, California

Aerojet-General Corporation
Materials & Fabrication Div.
Sacramento, California

Aerospace Industries Assn.
Los Angeles, California - 2

Air Material Command
Wright-Patterson A.F.B., Ohio

Air Research & Dev. Center
Baltimore, Maryland

Allegheny Ludlum Steel Corp.
Brackenridge, Pennsylvania

Allegheny Ludlum Steel Corp.
Watervliet, New York

Allied Chemical Corporation
General Chemical Company Div.
Morristown, New Jersey

Alloyd Corporation
Cambridge, Massachusetts

A.M.C.Ballistic Missiles Center
Los Angeles, California

Arcturus Mfg. Corporation
Venice, California

Armed Services Techn. Info. Agency
Arlington, Virginia

Argonne National Laboratory
Argonne, Illinois

Armour Research Foundation
Chicago, Illinois

Health & Safety Laboratory
U.S.A.E.C.-N.Y. Operations Office
New York, New York

U.S.A.E.C. Research Division
Germantown, Maryland

Atlantic Research Corporation
Alexandria, Virginia

Babcock & Wilcox Company
Beaver Falls, Pennsylvania

Battelle Memorial Institute
Columbus, Ohio - 3

Bell Aerosystems Company
Buffalo, New York

Bell Helicopter Corporation
Fort Worth, Texas

Bell Telephone Labs
Murray Hill, New Jersey

Bendix Aviation Corporation
South Bend, Indiana

Boeing Airplane Company
Aerospace Division
Seattle, Washington - 4

Boeing Airplane Company
Materials, Mechanics & Structures
Branch Seattle, Washington

Boeing Airplane Company
Wichita, Kansas

Professor Orlan W. Boston
Ann Arbor, Michigan

Mr. William L. Bruckhart
Pittsburgh, Pennsylvania

Mr. B. J. Brugge
Clayton, Missouri

Bjorksten Laboratory
Madison, Wisconsin

Bureau of Mines
Albany, Oregon

Bureau of Mines
Rolla, Missouri

Bureau of Naval Weapons
Washington, D. C.

California Institute of Technology
Pasadena, California

Cameron Iron Works
Houston, Texas

Canton Drop Forging & Mfg. Co.
Canton, Ohio

Carle Hospital Clinic
Urbana, Illinois

Cessna Aircraft Company
Wichita, Kansas - 2

Chance Vought Aircraft, Inc.
Dallas, Texas

Chromalloy Corporation
White Plains, New York

Cincinnati Milling Machine Co.
Cincinnati, Ohio

Clark Microanalytical Lab
Urbana, Illinois

Cleveland Pneumatic Tool Company
Cleveland, Ohio

Cleveland Tungsten, Inc.
Cleveland, Ohio

Clevite Research Center
Cleveland, Ohio - 2

Climax Molybdenum Company
New York, New York

Climax Molybdenum Co. of Michigan
Detroit, Michigan

Cochran Service Laboratories
Louisville, Kentucky

Convair
Fort Worth, Texas

Convair
Pamona, California

Convair Division
General Dynamics Corporation
San Diego, California - 2

Convair Astronautics Division
San Diego, California

Crucible Steel Co. of America
Midland, Pennsylvania

Curtiss-Wright Corporation
Buffalo, New York

Curtiss-Wright Corporation
Caldwell, New Jersey

Curtiss-Wright Corporation
Utica, Michigan

Curtiss-Wright Corporation
Wood Ridge, New Jersey

Department of Commerce
Office of Technical Services
Washington, D.C.

Denver Research Institute
Denver, Colorado

Douglas Aircraft Company, Inc.
El Segundo, California

Douglas Aircraft Company, Inc.
Long Beach, California

Douglas Aircraft Company, Inc.
Santa Monica, California - 2

Douglas Aircraft Company, Inc.
Tulsa, Oklahoma

Dow Chemical Company
Midland, Michigan

Eastern Stainless Steel Corporation
Baltimore, Maryland

E. I. du Pont deNemours & Company
Wilmington, Delaware

Eitel-McCullough, Inc.
San Bruno, California

Fairchild Engine & Airplane Corp.
Hagerstown, Maryland

Fairchild Engine & Airplane Corp.
Oak Ridge, Tennessee

Fansteel Metallurgical Company
North Chicago, Illinois

Firth Sterling, Inc.
Pittsburgh, Pennsylvania

Ford Motor Company
Dearborn, Michigan

Frankford Arsenal
Philadelphia, Pennsylvania

The Garrett Corporation
Los Angeles, California

General Electric Company
Cincinnati, Ohio - 3

General Electric Company
Lamp Division
Cleveland, Ohio - 2

General Electric Company
Evendale, Ohio

General Electric Company
Philadelphia, Pennsylvania

General Electric Company
Schenectady, New York

General Motors Corporation
Allison Division
Indianapolis, Indiana - 2

General Motors Corporation
Warren, Michigan

General Telephone & Electronics
Labs, Inc.
Bayside, New York

Giddings & Lewis Machine Tool Co.
Fond du Lac, Wisconsin

Goodman Manufacturing Company
Chicago, Illinois

Goodyear Aircraft Corporation
Akron, Ohio

Grumman Aircraft Eng. Corporation
Bethpage, Long Island, New York

Harvey Aluminum, Inc.
Torrance, California

Haynes Stellite Corporation
Kokomo, Indiana

Hiller Aircraft Corporation
Palo Alto, California

Hughes Aircraft Company
El Segundo, California

Hughes Aircraft Company
Culver City, California

Hughes Aircraft Company
Tucson, Arizona

Inspector of Naval Material
Chicago, Illinois

Jack & Heintz, Inc.
Cleveland, Ohio

Kelsey-Hayes Company
Utica, New York

Kennametal, Inc.
Latrobe, Pennsylvania

Kennecott Copper Corporation
Salt Lake City, Utah

Kropp Forge Company
Chicago, Illinois

Kulite Tungsten Company
Ridgefield, New Jersey

Ladish Company
Cudahy, Wisconsin

Lesi, Inc.
Grand Rapids, Michigan

Linde Company
Indianapolis, Indiana

Lockheed Aircraft Corporation
Marietta, Georgia

Lockheed Aircraft Corporation
Palo Alto, California - 2

Lockheed Aircraft Corporation
Synnyvale, California

Lockheed Aircraft Corporation
Van Nuys, California

Los Alamos Scientific Laboratory
Los Alamos, New Mexico - 2

Lycoming Division
Stratford, Connecticut

Marquardt Aircraft Company
Ogden, Utah

The Marquardt Corporation
Van Nuys, California - 2

The Martin Company
Baltimore, Maryland - 2

The Martin Company
Denver, Colorado

The Martin Company
Orlando, Florida

Massachusetts Inst. of Technology
Cambridge, Massachusetts

Materials Advisory Borad
Washington, D. C. - 2

McDonnell Aircraft Corporation
St. Louis, Missouri

Metcut Research Associates, Inc.
Cincinnati, Ohio

Metals & Residues, Inc.
Springfield, New Jersey

Mount Sinai Hospital
New York, New York

National Aeronautics & Space Admin.
Cleveland, Ohio

National Aeronautics & Space Admin.
Washington, D. C.

National Bureau of Standards
Washington, D. C.

Nat'l. Machine Tool Builders Assoc.
Washington, D. C.

National Research Corporation
Cambridge, Massachusetts - 2

Naval Air Material Center
Philadelphia, Pennsylvania

Naval Research Lab
Washington, D. C.

N. E. Materials Laboratory
Medford, Massachusetts

New York University
New York, New York

North American Aviation, Inc.
Canoga Park, California

North American Aviation, Inc.
Columbus, Ohio

North American Aviation, Inc.
Downey, California

North American Aviation, Inc.
Los Angeles, California

North American Phillips Co., Inc.
Lewiston, Maine

Northrop Aircraft Corporation
Hawthorne, California

The Norton Company
Worcester, Massachusetts

Office of Naval Research
Washington, D. C.

Office of Ordinance Research
Durham, North Carolina

Orbitec Corporation
Newport Beach, California

Oregon Metallurgical Corporation
Albany, Oregon

Phillips Metalonics
New York

Powder Alloys Corporation
Clifton, New Jersey

Pratt & Whitney Aircraft
Middletown, Connecticut

Radio Corporation of America
Camden, New Jersey

Raytheon Company
Andover, Massachusetts

Radio Corporation of America
Lancaster, Pennsylvania

Reactive Metals, Inc.
Niles, Ohio

Reduction & Refining Company
Kenilworth, New Jersey

Reisner Forge Company
Southgate, California

Rembar Company, Inc.
Dobbs Ferry, New York

Republic Aviation Corporation
Farmingdale, Long Island, New York

Rohr Aircraft Corporation
Chula Vista, California

Ryan Aeronautical Company
San Diego, California

Sandia Corporation
Albuquerque, New Mexico

Sandia Corporation
Livermore, California

Semicon of California
Watsonville, California

Shieldalloy Corporation
Newfield, New Jersey

Sikorsky Aircraft Division
United Aircraft Corporation
Stratford, Connecticut

Solar Aircraft Company
San Diego, California

Southern Research Institute
Birmingham, Alabama

Sowa Chemical Company
New York, New York

Speedring Corporation
Warren, Michigan

Sperry Gyroscope
Great Neck, Long Island, N. Y. - 2

Stackpole Carbon Company
St. Mary's, Pennsylvania

Stanford Research Institute
Palo Alto, California

Stauffer Metals Company
Richmond, California

Steel Improvement & Forge Company
Cleveland, Ohio

Super-Temp Engineering & Mfg., Inc.
Long Beach, California

Sylvania Electric Products, Inc.
Towanda, Pennsylvania

Taylor Forge & Pipe Works
Chicago, Illinois

Temco Aircraft Corporation
Dallas, Texas - 2

Temescal Metallurgical Corp.
Richmond, California

Thermionic Products Company
Plainfield, New Jersey

Thiokol Chemical Company
Denville, New Jersey - 2

Thiokol Chemical Company
Brigham City, Utah

Thompson-Ramo-Wooldridge, Inc.
Cleveland, Ohio - 3

Tufts University
Medford, Massachusetts

Union Carbide Metals Company
Niagara Falls, New York

Union Carbide Europa
Geneva, Switzerland

Union Carbide Nuclear Corp.
Oak Ridge, Tennessee - 2

United Aircraft Corporation
East Hartford, Connecticut

University of California
Livermore, California

University of California
Los Angeles, California

U. S. Army Chemical Corps
Fort Detrick, Maryland

U. S. Army Ordinance Corps
Dover, New Jersey

U. S. Army Ordinance Corps
Watervliet, New York

U. S. Naval Ordinance Test Station
China Lake, California

Vanadium Alloys Steel Company
Latrobe, Pennsylvania

Vitro Labs
West Orange, New Jersey

Wah Chang Corporation
Albany, Oregon

Wah Chang Corporation
Glen Cove, New York

Watertown Arsenal Lab
Watertown, Massachusetts - 2

Watervliet Arsenal
Watervliet, New York

Westinghouse Electric Corporation
Blairsville, Pennsylvania

Westinghouse Electric Corporation
Bloomfield, New Jersey

Westinghouse Electric Corporation
Kansas City, Missouri

Westinghouse Electric Corporation
Pittsburgh, Pennsylvania

Aeronautical Systems Center
Wright-Patterson A.F.B., Ohio

Wright Air Development Division
Wright-Patterson A.F.B., Ohio

Directorate of Resources
Wright-Patterson A.F.B., Ohio

Wright-Air Development Division
Dayton, Ohio

Wyman-Gordon Company
North Grafton, Massachusetts

Lockheed California Company
Burbank, California

Lockheed M & S Company
Sunnyvale, California

Aerospace Corporation
El Segundo, California