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A STUDY OF THE EFFECTS OF ADDITIVES ON
SINTERED TUNGSTEN POWDER COMPACTS

by

C. E. Williams and V. R. Friebe

THE DOW CHEMICAL COMPANY
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ABSTRACT

The effect of nickel, palladium, and uranium oxide additions on sintering and mechanical properties of isostatic-pressed tungsten powder compacts was investigated. A comparison was also made between slip casting and isostatic pressing for tungsten fabrication.

Nickel and palladium lowered the sintering temperature. Uranium oxide increased the mechanical properties. The diametral-compression test for measuring relative tensile strengths was evaluated and used during the investigation. Electron fractography was used to study the fractures.

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INTRODUCTION

The investigation was initiated to develop a simple technique for fabricating small complex items with good mechanical strength from tungsten. Tungsten is normally sintered at temperatures over 2750°C. It was necessary to develop a technique using conditions available with existing laboratory furnaces which can operate at temperatures up to 1750°C with a hydrogen atmosphere. Isostatic pressing was selected as the main forming method because of the ease of fabricating geometrically complex shapes.

The addition of nickel^(1,2) and palladium⁽³⁾ to tungsten powder to reduce the sintering temperature is a well-known technique. The effects of these additions on the mechanical properties have not been fully explored. Brophy, et al., measured the effect of powder preparation, amount of nickel addition, and firing time on the transverse rupture strength of tungsten powder.⁽⁴⁾ On the firing time, for example, they found that 0.25 percent nickel coated on the tungsten particles gave transverse rupture strengths of 37,100 psi after 10 minutes and 50,300 psi after 480 minutes at 1100°C. In the present work we have explored the effects of both nickel and palladium additives on tensile strength. As grain-growth lowers strength, the effect of adding uranium oxide as a grain-growth inhibitor was tested.

Diametral-compression testing was chosen as the test method because it minimizes surface effects and the test pellets are easier to make than tensile bars because of their simple geometry.^(5,6) While this test was

(1) Vacek, J., "On Influencing the Sintering Behavior of Tungsten," (German), Planseeber. Pulvermet., 7, 6 (1959).

(2) Brophy, J. H., Shepard, L. A., and Wulff, J., International Symposium on Powder Metallurgy, W. Leszynski, ed., New York, Interscience, 1961, p 113.

(3) Brophy, J. H., Hayden, H. W., Prill, A. L., and Wulff, J., The Investigation of the Activated Sintering of Tungsten Powder, Report of Investigation AD 401528, February 1963.

(4) Brophy, J. H., Hayden, H. W., and Wulff, J., "The Sintering and Strength of Coated and Co-reduced Nickel Tungsten Powder," AIME Transactions, 221, 1225 (1961).

(5) Rudnick, A., Hunter, A. R., and Holden, F. C., "An Analysis of the Diametral-Compression Test," Materials Research and Standards, 3, No. 4, 283 (1963).

(6) Spriggs, R. M., Brissette, L. A., and Vasilos, T., "Tensile Strengths of Dense Polycrystalline Ceramics by the Diametral-Compression Test," Materials Research and Standards, 4, No. 5, 218 (1964).

developed for testing non-ductile ceramic materials, tungsten is also brittle enough to break in tension under diametral pressure.

PROCEDURE

One batch of tungsten powder was used during this investigation. Electron microscopy showed that the particle size range was 0.1μ to 0.8μ and that the particles were generally angular. The chemical analysis provided by the tungsten supplier is shown in Table I.

TABLE I
SEMI-QUANTITATIVE ANALYSIS OF THE TUNGSTEN POWDER

<u>Element</u>	<u>w/o</u>	<u>Element</u>	<u>w/o</u>
Mo	0.005-0.05	Al	N.D.*
Si	<0.01	Ti	N.D.
Fe	<0.01	Cr	N.D.
Cu	<0.01	Mn	N.D.
Ni	<0.01	B	N.D.
Ca	<0.01	V	N.D.
Mg	<0.01	Zn	N.D.
Na	<0.01	Zr	N.D.
K	<0.01		

* Not detected.

The powder was isostatically pressed into bars approximately 1 inch by 1/2 inch by 7 inches. The pressing was done at 30,000 psi in latex pressing bags. No binders were added. The bars were machined into rods which were then cut to make pellets 0.45-inch long by 0.45 inch in diameter.

Slip casting of the pure tungsten was done using the method developed at Los Alamos Scientific Laboratory.⁽⁷⁾ The method involved dry milling the powder to develop an oxide layer, screening, suspending the powder in water, and casting the suspension in plaster molds.

The oxide layer was necessary to get suspension in water. No additives are necessary to make the powder stay in suspension. The slip-cast cylindrical pellets were about 1/2 inch by 1/2 inch.

The nickel and palladium were added to the tungsten powder by means of aqueous solutions of the nitrate and chloride, respectively. After drying the

(7) Private communication, S. D. Stoddard, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

slurries, the $\text{Ni}(\text{NO}_3)_2$ and PdCl_2 coatings on the tungsten particles were reduced to the metal elements by the technique of Brophy, et al.,⁽⁴⁾ by heating to 800°C in a hydrogen atmosphere for 30 minutes. The resultant powder was screened to partially break up the agglomerates, and then pressed. Attempts to slip-cast tungsten with the additives failed as the additives upset the rheology of the slip.

Uranium oxide was added as the grain-growth inhibitor. Depleted UO_2 was used rather than ThO_2 , which is used commercially, due to Health Physics considerations. The UO_2 was wet ball-milled 48 hours to reduce the particle size from 8μ to 0.05 to 0.3μ . The UO_2 suspension was added during the blending step to give 2 w/o UO_2 in the final dried product.

The pure tungsten pellets were fired at 1750°C for 8 hours in hydrogen. A dew point of $+20^\circ\text{C}$ was maintained. The pellets with additives were fired at 1100°C for 1 hour, and hydrogen with a dew point of -50°C was used as the atmosphere. The difference in dew point was a consequence of using two different sintering furnaces. The high temperature furnace which was required for sintering pure tungsten operates at a higher dew point than the low temperature furnace.

After firing the pellets, the ends of the slip-cast pellets were ground parallel before testing. The ends of the machined isostatic-pressed pellets remained parallel during firing.

The diametral-compression tester is shown in Figure 1. Light cardboard pads were used above and below the pellets to even out the applied stress.⁽⁵⁾ The load was applied at a constant rate of 3000 lb/min in the direction of the diameter and not the axis of the cylindrical samples. Most of the pellets broke in tension by means of triple-cleft fractures. The tensile strength was calculated, using the formula:⁽⁶⁾

$$m = \frac{2p}{\pi dt}$$

p = applied load
d = specimen diameter
t = specimen thickness
m = maximum tensile stress.

(4) Brophy, J. H., loc. cit., p 1.

(5) Rudnick, A., loc. cit., p 1.

(6) Spriggs, R. M., loc. cit., p 1.

Electron microscopy techniques were used to study the modes of fracture, grain size, and the distribution of the additive and oxide phases. The replicas were two-stage cellulose-acetate carbon shadowed at 30° with platinum-carbon.

RESULTS AND DISCUSSION

Figure 2 shows typical examples of the modes of fracture observed on the end view of the small cylindrical samples. The compressive load was applied parallel to and at the line of the main fracture. The stress distribution was such that the samples literally "popped apart" along the loaded diameter where the tensile stresses were at a maximum. The fractures are typical of the tensile fractures observed with ceramics. (5)

Figure 2d shows the normal tensile fracture. The triple-cleft mode of fracture may be the result of a secondary compressive loading due to the sudden release of the stored energy of the testing machine, causing subsequent tensile fractures of the two sections present after the initial tensile failure. (6)

A 99.5 w/o alumina ceramic was also tested by the diametral-compression method and the results showed excellent agreement with data in the literature.

A few samples failed by a compressive shear fracture which resulted in simple crushing of the samples. Data from these samples were not used in this report.

Table II shows the physical and mechanical property data.

The isostatic-pressed pure tungsten had a relatively low density due to being sintered at 1750°C, which was 1000°C below the normal sintering temperature without additives. It was still stronger than even the commercial tungsten products. The slip-cast pure tungsten had a larger average grain size than the isostatic-pressed tungsten, as shown in Figures 3 and 4, and it had a considerably lower ultimate tensile strength. The larger grain

(5) Rudnick, A., loc. cit., p 1.

(6) Spriggs, R. M., loc. cit., p 1.

TABLE II

PHYSICAL AND MECHANICAL PROPERTY DATA

Description	Tensile Strength (psi)	(N)	Std. Dev.	Confidence Limits for Mean - 95%		Density (g/cm)	Hardness (R _A)
				Upper (psi)	Lower (psi)		
Pure W Isostatic Pressed	43,300	15	5100	46,100	40,473	18.3	67
Pure W Slip Cast	13,600	20	2300	14,700	12,500	18.1	65
W + 0.25 w/o Ni Isostatic Pressed	13,900	16	1400	14,700	13,100	18.9	64
W + 0.25 w/o Pd Isostatic Pressed	16,400	18	2900	17,800	14,900	19.0	69
W + 0.25 w/o Ni + 2.0 w/o UO ₂ , Isostatic Pressed	20,600	19	2900	22,000	19,200	18.5	71
Swaged Pure W Rod Diametral Test	31,900	8	3900	35,200	28,700	--	69
Uniaxial Tensile Test	139,000	--	--	--	--	19.1	--
Thoriated W Electrode Diametral Test	27,700	8	6300	32,900	22,500	18.9	69
Uniaxial Tensile Test	103,000	--	--	--	--	--	--

Mean - Simple arithmetical average of the data.

(N) - Number of samples.

Standard Deviation - A statistical measure of the variation of the individual data points from the mean.

Confidence Limits for Mean - If another similar set of (N) samples were tested, 95 percent of the time the mean would be in the range expressed by the upper and lower limits.

size of the slip-cast tungsten was probably due to the additional oxide intentionally formed during the process. Tungsten oxide accelerates grain growth in powder-pressed tungsten.

The small particles apparent in isostatic-pressed tungsten in Figure 3 are believed to be tungsten particles which have had little, if any, grain growth. The particles appeared metallic and their size was in the range measured for the original tungsten powder. Similar small particles, and holes from pull-out of particles, are in the slip-cast tungsten in Figure 4. Well-developed faceting is present on a large grain and some smaller particles in Figure 4.

The nickel and palladium additions produced fair mechanical properties and excellent densities even though they were sintered for a much shorter time and at only 1100°C instead of 1750°C. The palladium addition produced stronger material than the nickel addition. It has been reported that palladium additions result in higher densities than nickel additions, but no data was given on comparative mechanical properties.⁽³⁾

Figures 5 and 6 show the intergranular mode of fracture and large grain size with the nickel addition as well as the uniform nickel grain-boundary phase. Nickel and palladium are both well-known for increasing grain growth in tungsten. Figure 6 shows an example of what was believed to be a thermally-etched void. What appears to be a crack was actually a tear in the replica.

Figures 7 and 8 are electron fractographs of tungsten with the 0.25 w/o palladium addition. The grain size was quite large due to the effect of the palladium. The palladium phase appears to spread out from the grain boundaries over parts of the grains. Since the fracture was intergranular, the palladium phase which appears in the grains was actually still between grains. The palladium may not have formed a complete coating on each tungsten grain.

The "river pattern" in Figure 7 could be due to a cleavage mode of fracture through the palladium phase at the boundaries.⁽⁸⁾ Areas of the grain-boundary phase in Figure 8 exhibit either slip lines or a cleavage-type

(3) Brophy, J. H., loc. cit., p 1.

(8) Low, Jr., J. R., Fracture, B. L. Averbach, et al., ed., Cambridge, MIT Press, 1959, pp 68-90.

fracture. This supports the supposition that the "river patterns" in figure 7 are due to a cleavage fracture through the grain-boundary phase.

All of the fractures had a few areas of transgranular fracture. Figure 9 shows an area of transgranular fracture with a twist boundary where a change in the density of cleavage steps occurred.⁽⁸⁾

The addition of 2.0 w/o UO_2 increased the properties of the tungsten with the nickel additive as shown in Table II. The UO_2 may have acted as either a grain-growth inhibitor or by dispersion strengthening or both. Figure 10 shows the dispersion of oxide particles. The larger grains in Figure 10 are considerably larger than the average grain size and should not be considered as typical. The UO_2 addition in Figure 10 affected the morphology and continuity of the nickel grain-boundary phase when compared to tungsten with the nickel additive in Figures 5 and 6.

The diametral-compression test proved satisfactory for a fast comparative method for determining relative tensile strengths for powder-pressed tungsten with easily fabricated samples of simple geometry. The tensile strength obtained by the diametral-compression test appeared to be low by a factor of four on the basis of the diametral-compression test data and the uniaxial tensile data for commercial swaged tungsten rod and thoriated tungsten electrode. As mentioned previously, the diametral-compression test was used on a ceramic and the results agreed with data in the literature. The low tensile strength values for powder-pressed tungsten may have been due to a slight degree of ductility in comparison to ceramics.

CONCLUSIONS

1. The diametral-compression test is an excellent method for the evaluation of tungsten powder metallurgy processes.
2. The isostatic-pressing process produces higher mechanical properties than slip-casting for pure tungsten.

The addition of 0.25 w/o nickel or palladium allows lower sintering temperatures and increases the density but decreases the tensile strength.

(8) Low, Jr., J. R., loc. cit., p 6.

4. Palladium is a more effective additive than nickel for sintering tungsten.
5. The addition of 2 w/o UO_2 to tungsten - 0.25 w/o nickel increased the strength and hardness.

ILLUSTRATIONS

Figure 1. DIAMETRAL-COMPRESSION FIXTURE WITH TUNGSTEN CARBIDE ANVILS. (FULL SCALE)

Figure 2a. TRIPLE-CLEFT

Figure 2b. MODIFIED TRIPLE-CLEFT

Figure 2c. MODIFIED TRIPLE-CLEFT

Figure 2d. NORMAL TENSILE

Figure 2. TYPICAL MODES OF FRACTURE (6X)

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Figure 3. ELECTRON FRACTOGRAPH OF ISOSTATIC-PRESSED TUNGSTEN.
TYPICAL INTERGRANULAR FRACTURE. (5600X)

Figure 4. ELECTRON FRACTOGRAPH OF SLIP-CAST TUNGSTEN WITH A GRAIN SHOWING EXCELLENT FACETING. TYPICAL INTER-GRANULAR FRACTURE. (5600X)

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Figure 5. ELECTRON FRACTOGRAPH OF W-0.25 w/o Ni. TYPICAL INTER-GRANULAR FRACTURE AND GRAIN BOUNDARY PHASE. (5600X)

Figure 6. ELECTRON FRACTOGRAPH OF W-0.25 w/o Ni. UNIFORM GRAIN BOUNDARY NICKEL PHASE PLUS A THERMALLY-ETCHED VOID. (24,000X)

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Figure 7. ELECTRON FRACTOGRAPH OF W-0.25 w/o PD. TYPICAL INTER-GRANULAR FRACTURE AND GRAIN BOUNDARY PHASE. (5600X)

Figure 8. ELECTRON FRACTOGRAPH OF W-0.25 w/o Pd. TYPICAL INTER-GRANULAR FRACTURE WITH CLEAVAGE STEPS OR SLIP LINES IN THE GRAIN BOUNDARY PHASE. (5600X)

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Figure 9. ELECTRON FRACTOGRAPH OF W-0.25 w/o Pd. RARE TRANS-GRANULAR FRACTURE WITH A "TWIST" BOUNDARY. (5600X)

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Figure 10. ELECTRON FRACTOGRAPH OF W-0.25 w/o Ni WITH 2.0 w/o UO_2 . TYPICAL INTERGRANULAR FRACTURE AND GRAIN BOUNDARY PHASE. (5600X)

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