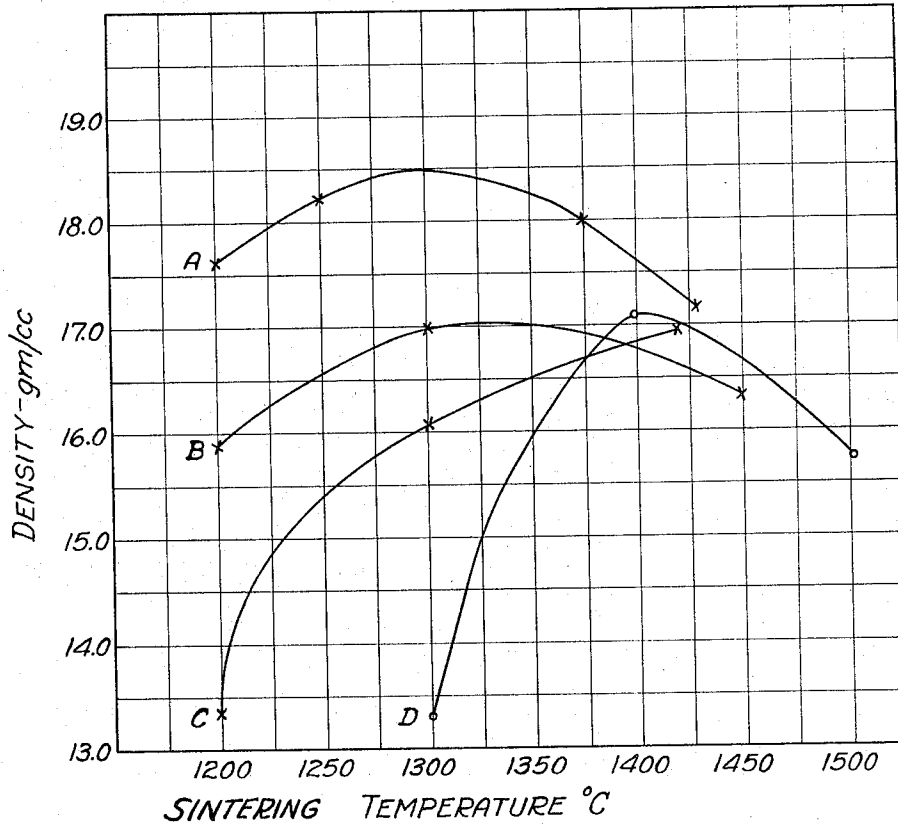


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POWDER-METALLURGICAL TUNGSTEN-BASE ALLOY
AND METHODS OF MAKING SAME
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**POWDER-METALLURGICAL TUNGSTEN-BASE
ALLOY AND METHODS OF MAKING SAME**

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The present invention relates to powder-metallurgical tungsten-base alloys of improved sinterability and to methods of producing such alloys.

In the past, many methods have been utilized for activating the sintering of tungsten metal powder compacts. Sintering enhancement techniques have generally fallen within three categories: first, controlling the sintering atmosphere such as by adding halogen-containing gases; second, controlling the tungsten powder characteristics including purity and particle size and shape; and third, by the use of small amounts of metallic or salt additions to the powder. In the third category, published literature indicates that the ferrous group metals iron, nickel and cobalt are far superior to other metals. However, the ferrous group metals are often not desired as residual alloying additives in sintered tungsten articles, especially those intended for very high temperature uses.

Pressed-and-sintered articles can sometimes be used without further fabrication such as in the form of heat sink disks used in semiconductor products, electrodes for melting, and as crucibles or other products. For some uses, it is desirable to be able to forge or otherwise deform the pressed-and-sintered articles to make a final product.

It is an object of the present invention to provide powder-metallurgical tungsten-base alloys with improved sintering characteristics.

It is another object of the invention to provide methods for sintering tungsten-base powder-metallurgical alloy compacts to achieve improved densification under given sintering conditions and thereby to allow more economical production of pressed-and-sintered tungsten articles.

The single figure of the drawing is a graph showing some of the relations of various composition and process parameters in the practice of the invention.

Briefly stated, the present invention in one embodiment provides pressed-and-sintered tungsten-base alloys containing from a small but effective amount to enhance sintering to about 5% by weight manganese. (Percentages herein are by weight except where specified otherwise.) The manganese is added in appropriate amounts as a metal powder to tungsten powder to enhance the sintering characteristics of the tungsten. Improvements in the properties of the sintered product also can result. The sintering takes place in the absence of reactive gases, meaning either in vacuum or in an atmosphere that is reducing or neutral relative to the compacts being sintered. By various combinations of sintering temperature within the range of approximately 1050–1700° C., or preferably about 1200–1400° C., with atmospheres or vacuums of various pressures, more or less of the manganese metal additive may be retained in the sintered product. By sintering at a high enough temperature in a sufficient vacuum, practically all of the manganese can be evaporated out of the compact after it has served its purpose in improving sintering. On the other hand, by using lower temperatures and higher pressures of non-reactive gases during sintering, larger proportions of the manganese additives may be retained in the alloy when such is desired. Alternatively, grain-growth-promoting additives such as aluminum, potassium and silicon used in the production of tungsten lamp wire, also may be present in

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the tungsten metal powder in amounts from zero up to small amounts effective to promote grain growth. Such additives aid in producing a product which, in the form of wire or sheet, would have enhanced grain growth characteristics such as to produce non-sag, non-offsetting structures. Furthermore, we have found that additions of up to about 0.3% sulphur to the powders significantly reduce the oxygen content of the sintered product, and additions of up to about 0.2% yttrium impart forgeability to the product.

Examples

Manganese metal in an amount of 3% provided in the form of electromanganese —50, +325 mesh powder in the Tyler screen series with impurities of 240 p.p.m. sulfur and 860 p.p.m. oxygen was added to tungsten metal powder of about 4.5 microns diameter containing grain growth promoting additives, and the resulting metal powder mixture was thoroughly blended. The tungsten powder with grain-growth-promoting additives was produced by techniques known in the art such as in the prior art discussed in Pugh et al. application S.N. 285,173, filed May 9, 1963 and assigned to the same assignee as the present application, now Patent 3,236,699, issued February 22, 1966. The mixture was pressed by a ram at a pressure of 12 tons per square inch to make an ingot having dimensions of $\frac{3}{8}$ x $\frac{3}{8}$ x 24 inches having a pressed density of 11.5 grams per cubic centimeter (gm./cc.), or about 60% of the full theoretical density. The ingot was subsequently sectioned to make a number of smaller samples, each having a $\frac{3}{8}$ x $\frac{3}{8}$ inch square cross section by 3 inches long. Sintering a sample from this ingot in hydrogen at 1150° C. for three hours resulted in the loss of 1.5% manganese from the sample. Sintering a similar sample at 1240° C. in vacuum for three hours resulted in the loss of all but 0.2% manganese. The latter sample had a density of 14.5 grams per cubic centimeter, 75% of theoretical density. A pure tungsten compact made in the same way and sintered at 1240° C. for three hours in hydrogen had a density of 11.5 grams per cubic centimeter or 60% of theoretical. Thus, sintering was greatly enhanced through activation by the manganese additive.

Other exploratory experiments were also conducted on the alloy to which 3% manganese had been added. Table I shows the results for vacuum sintering, and Table II shows similar results for hydrogen atmosphere sintering. A comparison of the two tables indicates that densification in a hydrogen atmospheres is more dependent on temperature than is densification in vacuum for alloys of the invention. This could perhaps be caused by evaporation of manganese. In Tables I and II, the notation <13.5 indicates that in preliminary screening testing of density, the specimen floated in liquid mercury, and therefore had a lower density than that of mercury, 13.5 gm./cc. Temperature measurements throughout this specification have an accuracy of about $\pm 25^\circ$ C.

TABLE I.—DENSIFICATION OF W-3% Mn SINTERED
3 HOURS IN VACUUM

Temperature (° C.):	Density (gm./cc.)
1180	<13.5
1200	<13.5
1240	14.5
1280	14.5
1350	14.6
1430	14.6
1500	14.6

TABLE II.—DENSIFICATION OF W-3% Mn SINTERED 3 HOURS IN HYDROGEN

Temperature (° C.):	Density (gm./cc.)
1150 -----	<13.5
1200 -----	<13.5
1310 -----	17.6
1430 -----	18.35
1500 -----	17.45
1600 -----	16.40

Similar experiments were conducted both in hydrogen and in vacuum on a similar alloy containing about 0.9%

the occurrence of the second phase, which appeared to be formed by melting during sintering. Tungsten and manganese may not be sufficiently soluble in each other for the second phase to be a tungsten-manganese eutectic. Various additions of sulphur, carbon, phosphorus and yttrium metals were made to tungsten metal powder containing varying amounts of manganese. Each of the additives was added as elemental powder and thoroughly blended. Table IV below shows the nominal compositions that were prepared, the sintering conditions and the resulting density after sintering.

TABLE IV

Alloy No.	Nominal Composition (Percent)	Sintering Conditions			Density (gm./cc.)
		Atmosphere	Time (Hrs.)	Temp. (° C.)	
8 -----	W, 1 Mn, .2S -----	H ₂	4	1,400	15.8
9 -----	W, 1 Mn, .2S -----	Vac.	1	1,900	15.8
10 -----	W, 2 Mn, .8 to .1C -----	Vac.	4	1,400	17.0
11 -----	W, 5 Mn, .3S -----	H ₂	4	1,400	17.6
12 -----	W, 5 Mn, .3S -----	H ₂	1	1,400	<13.5
13 -----	W, 2 Mn, .1S -----	H ₂	2	1,400	17.6
14 -----	W, 2 Mn, .2Y -----	Vac.	1	1,400	16.2
15 -----	W, 2 Mn, .1P -----	H ₂	2	1,400	17.6

manganese. None of the samples sintered at temperatures below 1600° C. had densities higher than 13.5 gm./cc. After sintering three hours at 1600° C. in hydrogen, a density of 13.7 gm./cc. was achieved. This is a somewhat higher density than could be expected for pure tungsten at 1800° C. sintered in hydrogen for three hours. Therefore, some degree of activation appears to have been achieved with 0.9% manganese.

It was also found that varying the cross section of the article to be sintered had an effect on the product. Compacts were made having a cross section of 7/8 x 5/8 inch with additions of from 0.5 to 10% manganese. Before sintering as described above, the powder was ram-pressed in a double-acting die with 12 tons per square inch pressure to form 7/8 x 5/8 x 24 inch ingots. Some of these ingots were cut into three inch lengths which were transferred to either a vacuum sintering furnace or a dry hydrogen atmosphere furnace for sintering at specified times and temperatures. The ultimate pressure of the vacuum furnace was 1×10^{-4} millimeters Hg, the dew point of the hydrogen furnace was about -80° F., and sintering temperatures were in the range of 1100 to 1500° C.

After sintering, density measurements were made on the sintered bodies. Oxygen and residual manganese additions were analyzed, and the microstructures were examined. Table III below shows the results of these tests.

TABLE III

Alloy No.	Percent Mn Addition	Sintering Conditions			Density (gm./cc.)	Analysis (Percent)	
		Atmosphere	Temp. (° C.)	Time (Hrs.)		O ₂	Mn
1 -----	0.5	H ₂	1,425	4	14.1	.284	.34
2 -----	0.5	H ₂	1,425	6	14.4	.237	.17
3 -----	1.0	H ₂	1,425	6	17.3	.232	.67
4 -----	3.0	H ₂	1,425	6	18.2	.156	1.10
5 -----	3.0	Vac.	1,425	4	16.9	.170	.50
6 -----	5.0	H ₂	1,425	1	17.9	.218	2.30
7 -----	10.0	Vac.	1,300	8	15.5	-----	-----

It can be seen that the degree of manganese retention is greater after positive-pressure sintering, due to less evaporation at the sintering temperature. The amount of retained manganese in these samples goes down to 0.17%, or about 0.1%.

A second phase was apparent under microscopic examination in many of the samples. An attempt was therefore made to deoxidize the material during sintering or otherwise remove whatever impurities might be causing

The additions of phosphorous and carbon neither gave any detectable deoxidation nor produced a forgeable product. However, the addition of 0.1% sulfur to the alloy having 2% manganese lowered the resulting oxygen content from 400 parts per million (p.p.m.) to 80 p.p.m. Also, the yttrium addition in alloy 14 provided a forgeable article. A sample of this alloy 0.550 inch thick was forged to 0.250 inch thick (a reduction in thickness of about 55%) at 1600° C.

A 3/8 x 3/8 x 3 inch sample of the 3% manganese alloy sintered in vacuum at 1280° C. for three hours was successfully forged about 40% after heating in hydrogen to 1600° C. The fabricability demonstrated in this test was judged superior to that of pure tungsten sintered under the same conditions.

One of the 24 inch long x 7/8 x 5/8 inch cross-section ingots was sintered (with manganese activation) at 1600° C. for one hour, then at 2500° C. for one hour, and subsequently subjected to self-resistance sintering at 2900° C. for 1/2 hour in hydrogen. This ingot was made from tungsten powder containing grain-growth promoting additives and known as "218 W" to which was added 0.5% Mn. The resulting ingot was rolled to sheet 0.030 inch thick and subjected to tensile and hardness testing. The results are shown in Table V below in comparison with results obtained from 218W, and the same material with which had been alloyed 3% rhenium and 10%

rhenium. These alloys and their preparation are described in the above-identified application of Pugh et al. The tensile and hardness testing was done at 200° C., with tensile testing at a speed of 0.01 inch per minute and a gauge length of 3/4 of an inch. The material was in a cold-worked condition and testing was done parallel to the rolling direction. U.T.S. k.s.i. means ultimate tensile strength in thousands of pounds per square inch, and 0.2%

Y.S. means the 0.2% offset yield strength. DPH means Diamond Pyramid Hardness.

TABLE V

Nominal Composition (Percent)	U.T.S., k.s.i.	0.2% Y.S., k.s.i.	Percent Elongation	Average Hardness (DPH), 10 Kg. Load
218W+.5 Mn.....	135	132	5.02	462
218W.....	150	146	3.19	480
218W+3Re.....	162	159	4.52	460
218W+10Re.....	195	191	4.47	510

It is significant to note that the alloy in Table V to which manganese had been added contained as residuals only about 10 p.p.m. manganese and 5 p.p.m. oxygen. Even so, the manganese had a significant favorable effect on ductility, with a slight lowering in tensile strength and hardness. Thus, it can be seen that alloys prepared by powder metallurgical means and sintered which retain very small amounts of manganese still show significant effects in their properties of the residual manganese.

The graph in the drawing shows the relationships of sintering temperature and resulting density with different manganese additions and with sintering done in both vacuum and hydrogen. Curve A is for an addition of 1% manganese with sintering done in hydrogen for 4 hours. Curve B is for additions of both 3 and 5% coarse manganese powder (average particle size about 120 micron) to tungsten powder sintered in vacuum for 4 hours. Curve C also applies to sintering of compacts containing 3 and 5% manganese in vacuum for 2 hours, but with the manganese supplied as a fine powder having a particle size of about 44 micron. Finally, Curve D shows the results achieved with additions of 2% manganese and 0.15% carbon with sintering done in vacuum for 2 hours. Curve D shows that, although these amounts of carbon are detrimental to sintering at low temperatures, equivalent preferred results can still be achieved at about 1400° C. Therefore, even this amount of carbon should be considered as an incidental impurity since it does not negate the activated sintering advantages of the manganese. Curves A, B and C demonstrate the improvements in sintering that have been obtained by manganese activation.

It will be appreciated by those skilled in the art that improved densities also can be obtained (1) with larger amounts of manganese activator, (2) with sintering done at higher temperatures or (3) for longer times, the three factors being inter-related, with density dependent on all three. An increase in one of the three factors will allow a corresponding decrease in the others to obtain equivalent results. We have found that, with appropriate selection of parameters, good sintering enhancement can be obtained with manganese additions of about 0.5% resulting in sintered articles containing down to about 0.1% manganese as a preferred embodiment of the invention.

In addition, it is now well known that the interaction of the electronic structure of two metals in an alloy can contribute greatly to the strength and ductility of the alloy. We consider it likely that interactions between the electronic structures of manganese and tungsten occur causing manganese in the claimed amounts to substan-

tially improve the strength and ductility properties of tungsten.

It is contemplated that this invention shall be interpreted as broadly as the true scope and spirit of the appended claims.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A powder-metallurgical, sintered, tungsten-base alloy consisting essentially of, by weight, from a small but effective amount to enhance sintering to about 5% manganese, from zero to about 0.3% sulfur, from zero to about 0.2% yttrium, and from zero to a small but effective amount of additives to promote grain growth, the balance tungsten and incidental impurities.

2. The alloy of claim 1 in which the manganese content is about 0.05% by weight.

3. The alloy of claim 1 in which the manganese content is about 0.5% by weight.

4. A powder-metallurgical, sintered, tungsten-base alloy consisting essentially of about, by weight, 0.5% manganese, and 0.01% sulfur, the balance tungsten and incidental impurities.

5. A powder-metallurgical, sintered, tungsten-base alloy consisting essentially of about, by weight, 0.5% manganese, and 0.05% yttrium, the balance tungsten and incidental impurities.

6. A process for producing sintered tungsten compacts more readily sintered than pure tungsten, said process comprising the steps of:

(a) preparing a mixture, by weight, of tungsten metal powder with from about 0.5% to about 10% manganese metal powder, from zero to about 0.3% sulfur, from zero to about 0.2% yttrium, and from zero to a small but effective amount of additives to promote grain growth,

(b) pressing the powder mixture into a green compact, and

(c) firing the green compact in the absence of a reactive gas at a temperature in the approximate range of 1050-1700° C.

7. The process of claim 6 in which the added manganese content is about 3% and the firing temperature is in the approximate range of 1250-1400° C.

8. The process of claim 6 in which the added manganese content is about 0.5% and the firing temperature is in the approximate range of 1250-1400° C.

9. The process of claim 6 in which the materials mixed with the tungsten metal powder are about, by weight of the mixture, 2% manganese and 0.1% sulfur.

10. The process of claim 6 in which the materials mixed with the tungsten metal powder are about, by weight of the mixture, 2% manganese and 0.2% yttrium.

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