

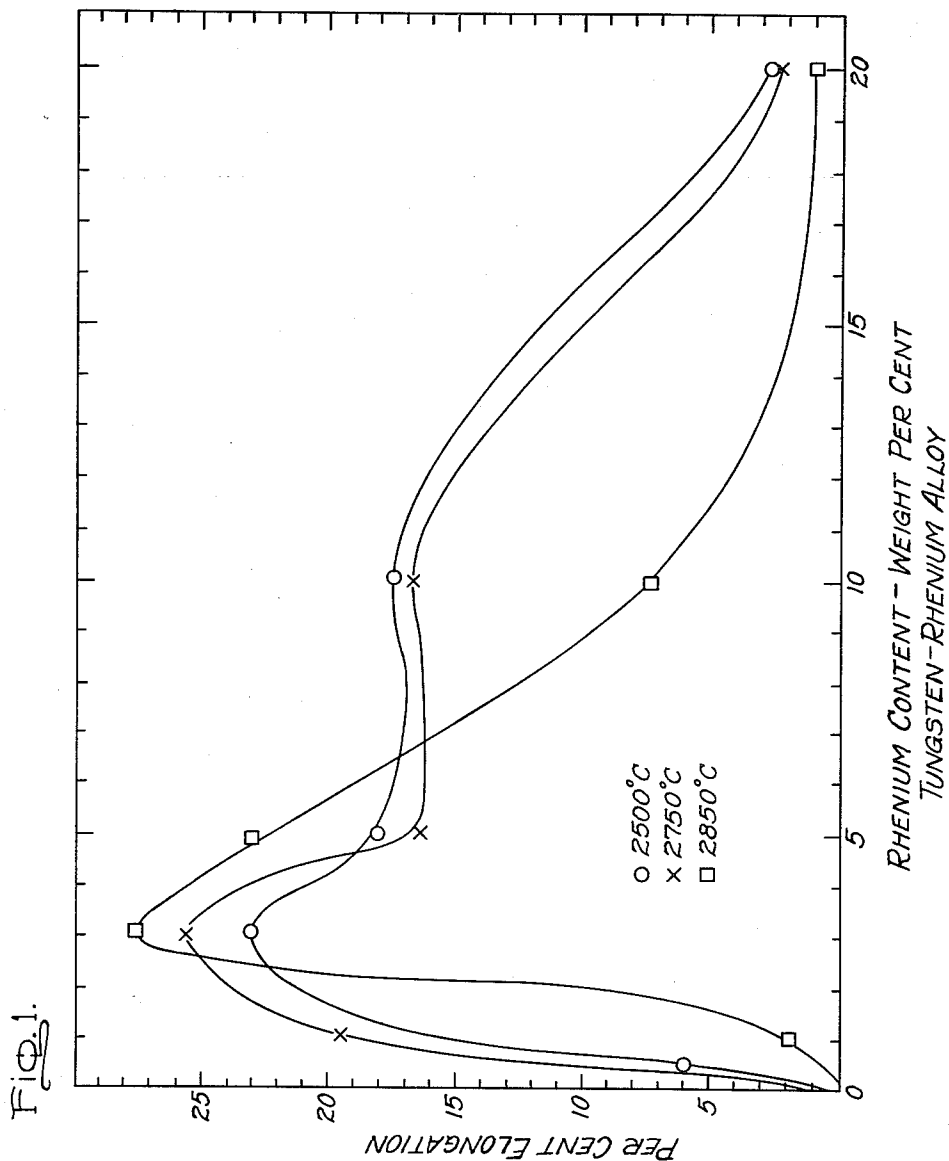
Feb. 22, 1966

J. W. PUGH ETAL
TUNGSTEN-RHENIUM ALLOYS

3,236,699

Filed May 9, 1963

4 Sheets-Sheet 1



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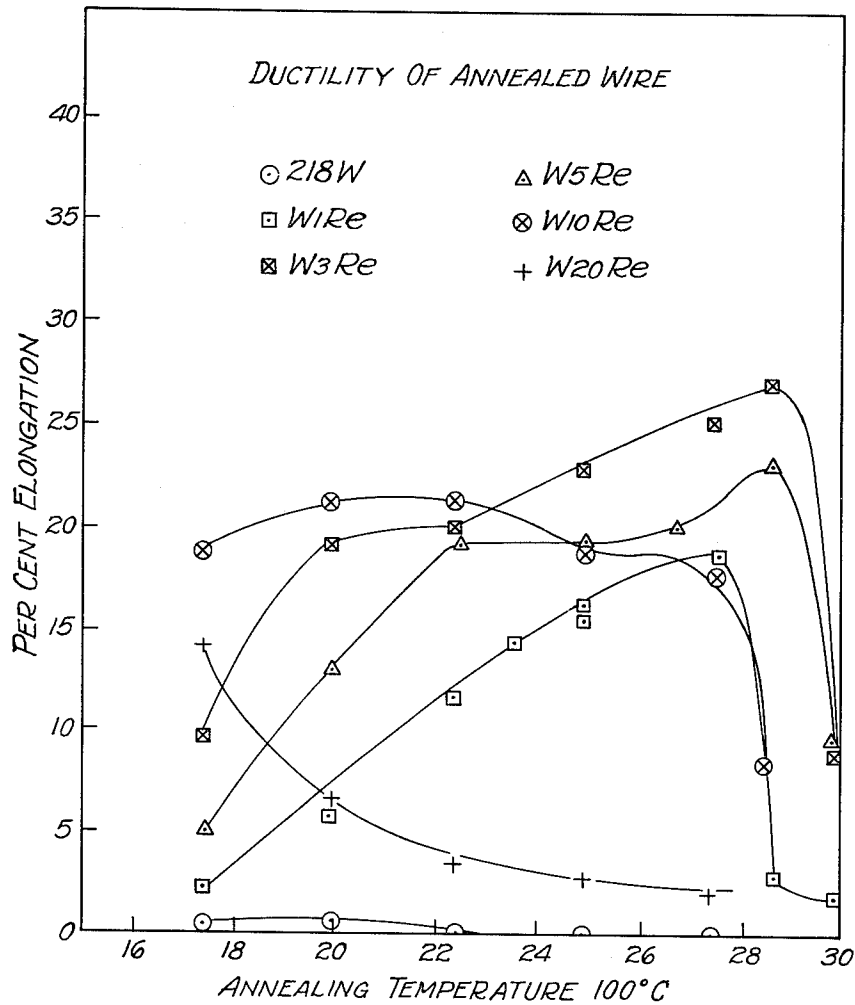
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4 Sheets-Sheet 2

FIG. 2.



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TUNGSTEN-RHENIUM ALLOYS

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4 Sheets-Sheet 3

FIG. 6.

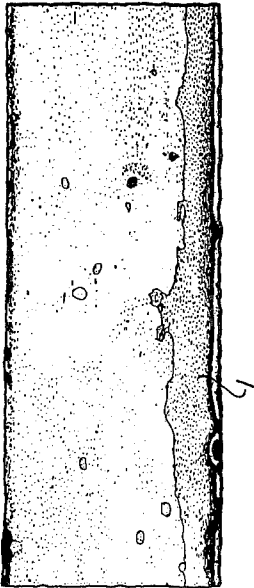


FIG. 7.

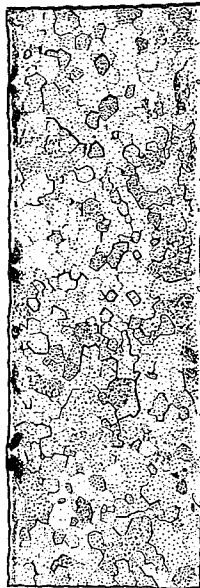


FIG. 8.

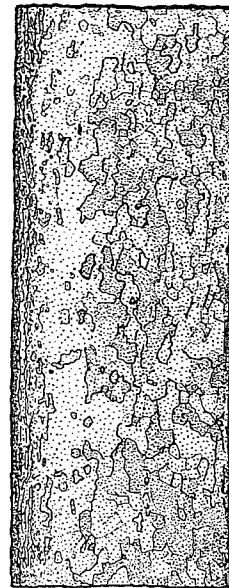


FIG. 3.



PRIOR
ART

FIG. 4.

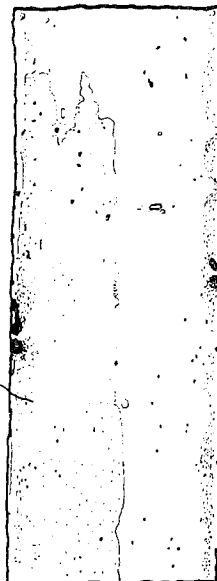


FIG. 5.



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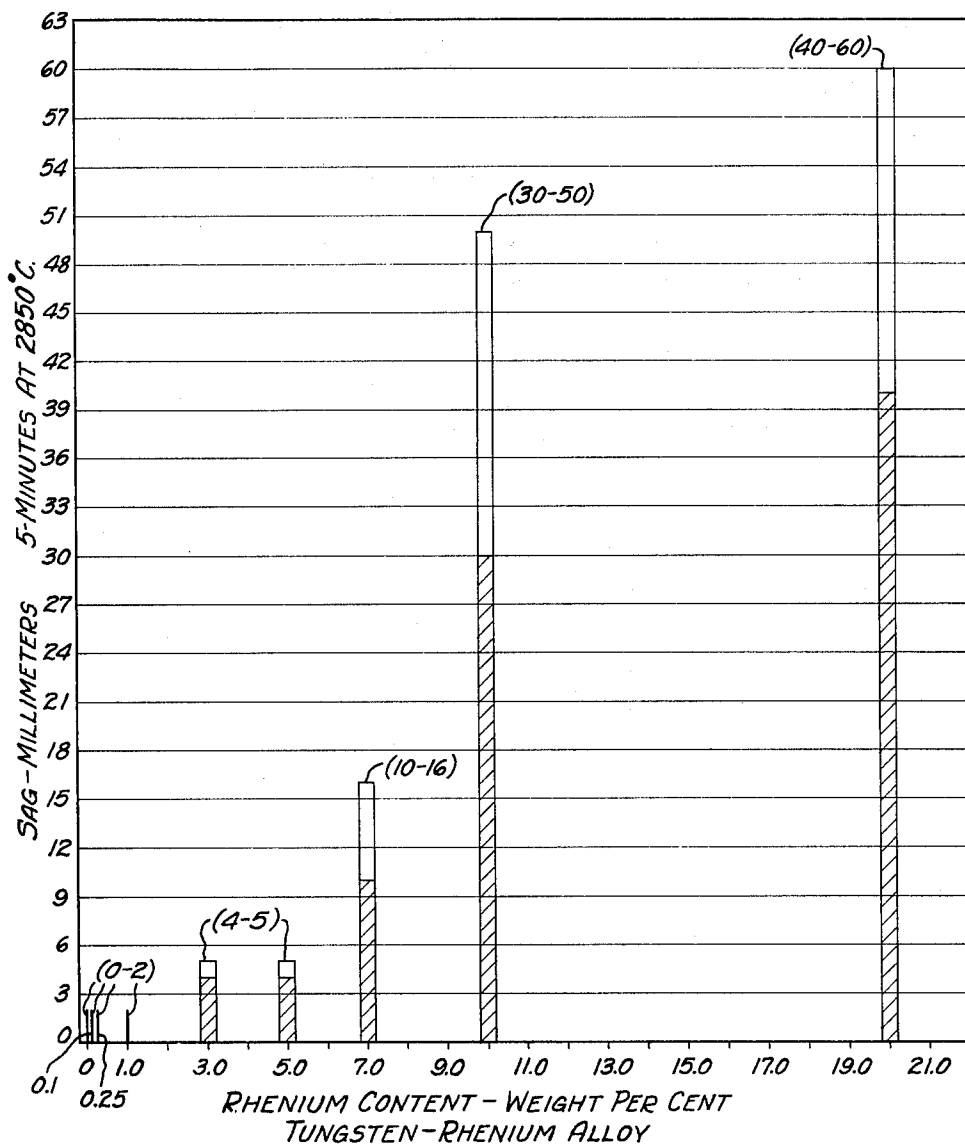
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TUNGSTEN-RHENIUM ALLOYS

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4 Sheets-Sheet 4

FIG. 9.



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3,236,699

TUNGSTEN-RHENIUM ALLOYS

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Filed May 9, 1963, Ser. No. 285,173
10 Claims. (Cl. 148—11.5)

This application is a continuation-in-part of and replaces application Serial No. 29,222, filed May 16, 1960, now abandoned, entitled, Tungsten-Rhenium Alloys, and assigned to the same assignee as the instant invention.

The present invention relates generally to alloys of tungsten and rhenium and especially to tungsten-rhenium alloys for use as heating or incandescible filaments in electrical devices and to filaments or wires made from such alloys.

Tungsten filament wire is customarily twisted, bent, coiled, formed or rolled into many different shapes, sizes and lengths for incorporation into lamps, vacuum tubes and other electronic devices. Once incorporated into a device, it is important that the filament wire maintain its form or position without sagging or deforming even when heated to incandescence. At the same time, the mounted filament must be able to withstand normal shocks and vibrations incident to shipping, handling and use of the device. These demands of manufacture and performance require that the filament be ductile so that it may be readily fabricated into many intricate shapes or coils for incorporation into such lamps or devices, that the filament exhibit non-sag qualities at incandescence to prevent deformation, and that the filament retain some ductility and strength at incandescence and after being heated to incandescence so as not to become so brittle and fragile as to break under normal usage.

The product of tungsten ore reduction procedures is a metal powder. The tungsten powder may be pressed into bodies and heated to form bars or ingots but these are hard and brittle, have a generally polycrystalline structure, and exhibit little ductility. As a result of early work by Coolidge, as disclosed in his Patent 1,082,933 dated December 30, 1913, it was found possible to heat treat and mechanically work such bodies at high temperatures such as by forging, swaging and sintering, to convert the crystalline structure into a fibrous, elongated grain structure. The mechanically worked, sintered bodies of fibrous structure are pliable and ductile and have sufficient tensile strength so that they may be drawn into wires and incandescible filaments for electric lamps. However, during the operation of such lamps, the tungsten filaments are at temperatures such that the tungsten tends to recrystallize and the filaments become brittle after such recrystallization. Further, when such filaments are used in the form of coils or coiled-coils, the turns of the coils tend to sag together and short-circuit themselves, among other disadvantages resulting from the deformation of the filament due to sagging.

A number of methods have been proposed for controlling the recrystallization and grain growth of the tungsten to produce a desired crystalline structure in, and desired properties of, such filaments after recrystallization. It is well-known that such properties as tensile strength and electrical resistance, which have been developed during the working of the tungsten body into the form of a ductile tungsten filament, are completely changed by recrystallization when the filament is heated to an incandescent temperature in an electric lamp. To obtain any particular structure in, and properties of such filaments, it is, of course, necessary to control the process of recrystallization. The known methods for controlling the process of recrystallization of incandescible filaments include both heat treatments during rolling, swaging and

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drawing of the tungsten prior to recrystallization of the filament, and the introduction of various additives before the ingot is formed by pressing and sintering. The effect of specific heat treatments and additives on tungsten prior to recrystallization does not indicate what the effect thereof will be on the structure and properties of the tungsten after recrystallization.

Additives and methods for producing coiled tungsten filaments for electric lamps, which filaments do not deform, elongate or sag substantially between their supports in a lamp after the filament has been recrystallized, and which are substantially free from "offsetting" caused by slip on the crystal boundaries, are disclosed and claimed in Patent 1,410,499—Pacz, patented May 21, 1922 on an application filed February 20, 1917. Such filaments are used extensively in the form of coils and coiled coils in many types of lamps. One of the tungsten compositions mentioned in this Pacz patent is designated as "218" metal and is made by reducing in a hydrogen atmosphere a tungsten oxide intimately associated with commercial grade chemicals, including Na_2CO_3 , K_2CO_3 , NaNO_3 and silicic acid, and thereafter pressing the mixture in powder form into ingots which are sintered and then mechanically worked down to the form of wire by methods including hot swaging and drawing into the form of lamp filaments, as described in the Coolidge patent referred to above. The filament wire so produced is sufficiently ductile for coiling, as mentioned above. The chemical treatment of the tungsten oxide is known in the art as "doping" and the tungsten produced by the process is frequently called "doped tungsten."

The non-sag and non-offsetting characteristics of filaments made in accordance with the Pacz teachings are secured during the heat treatment, described below, of the filaments mounted in the lamps. Neither before nor after the heat treatment can presently known chemical analysis techniques disclose the presence of the additives above the background level of such substances normally present as impurities in non-doped tungsten. During the sintering of the ingot the additives are removed almost in entirety, presumably by volatilization. However, present theory assumes that residual, small amounts of Al, K and Si atoms, incorporated into the tungsten crystal lattice in some manner not fully understood, control recrystallization to produce a non-sagging and non-offsetting structure.

After the coiled filaments of the kind described above are mounted on supports in the lamp and the lamp envelope has been sealed, the filament is heat treated by passing an electric current therethrough to obtain the non-sag characteristics. During this heat treatment the fibrous structure of the ductile coiled tungsten filament is changed to a recrystallized structure. Usually the heat treatment is done at the first light-up of the sealed lamp and is called "flashing" or "aging." This treatment includes operating the lamp for short intervals at progressively higher voltages starting below the normal lamp operating voltage and ending at or slightly above the normal operating voltage of the lamp.

The filament, after recrystallization has occurred, loses its ductility and becomes brittle, though it does not sag appreciably on its supports under the force of gravity after recrystallization and is substantially free from offsetting during lamp life. The heat treatment thus stabilizes the structure of the filament.

The brittleness of the filament after recrystallization precludes flashing or aging thereof before it is mounted on its supports in a lamp or other electrical device, though in many cases it would be highly advantageous to do so to facilitate manufacture of the lamp or electric device. For example, some provision must be made to prevent

the deformation or sagging of the mounted coiled filament during the hot interval before the filament loses its ductility and before the recrystallized structure has been obtained, inasmuch as during this hot interval the rigidity of the wire is rather low. For this purpose an elongated coiled filament usually is positioned horizontally in a lamp and supported along its length at numerous spaced-apart points, the number and spacing of which is determined by the tendency of the filament to sag during this period of weakness while aging.

Further, the cooling effect of the filament supports frequently results in failure of recrystallization at and adjacent to the points of contact of the filament with its supports so that the filament structure has a sharp transition from a recrystallized structure to a fibrous structure at the points of support. Such sharp transition portions of the filament are more brittle, are weaker and tend to fracture under service conditions more frequently than other portions of the filament, thus terminating the useful life of the lamp.

It now is known that, on recrystallization of the filament, various additives, such as thoria, restrain grain growth, and that other additives, such as aluminum, potassium and silicon, produce exaggerated grain growth as compared with the structure developed by coiled filaments of tungsten free from such additives. Of course, the "218" metal of the Pacz patent includes as additives to the tungsten oxide powder formed into an ingot, silica and alkali metal which produce exaggerated grain growth in the coiled non-sag filaments produced from wire made by the Pacz method. The grain growth proceeds primarily in the longitudinal direction of the wire and results in coarse, interlocked grains and irregular grain boundaries which form, on the average, very small angles with the surfaces of the wire. This grain structure is quite effective in preventing sag, which is primarily a creep process, and offsetting due to slip in grain boundaries forming large angles with the wire surface. Similar effects might also be achieved in thin sheet and other bodies of narrow cross section such as extruded tubes and irregularly shaped articles. Filaments for electric lamps and electronic tubes which are operated at temperatures above the temperatures at which recrystallization occurs, and made by techniques based on the teachings of the Coolidge and Pacz patents mentioned above, have been in commercial use for more than 30 years. The Pacz designation "218" is presently used for K, Si, Al doped tungsten which develops a non-sag, non-offsetting structure when recrystallized as a filament.

Although, as previously mentioned, the Pacz 218 tungsten wire has provided a satisfactory lamp filament over the course of the years, we have found that its properties will be substantially improved in terms of cold ductility and sag resistance at operating temperatures if the tungsten is alloyed with small quantities of rhenium.

Accordingly, it is an object of the present invention to provide a tungsten-rhenium alloy providing exaggerated grain growth and retention of ductility after recrystallization.

Another object of the invention is to provide filaments of the above type which are of vastly improved ductility after recrystallization than are present filaments of this type known in the art and which also are characterized by good resistance to sag and off-setting.

Still another object of the invention is to provide such filaments having a higher recrystallization temperature than present filaments.

A further object of the invention is to provide such filaments which are ductile as recrystallized and resistant to sag and offsetting after operation in electrical devices at temperatures causing embrittlement of prior filaments of this type and which are useful in electrical devices generally.

A still further object of the invention is to provide a method of increasing the recrystallization temperature

and the ductility of such filaments while retaining the necessary non-sag and non-offsetting characteristics. Further objects and advantages of the invention will appear from the following description of species thereof and from the appended claims.

Briefly, according to one aspect of the present invention, embrittlement by recrystallization of filaments made in accordance with present commercial techniques and based on the teachings of Pacz and Coolidge is prevented or largely avoided when rhenium is incorporated in the form of metal powder or in other forms in certain limited small amounts, disclosed below, into the material from which the ingot is formed, which material includes additives which impart sag-resistance and prevent offsetting in recrystallized filaments. The rhenium metal increases the ductility of the filament both after annealing and after recrystallization. It also raises the temperature at which recrystallization occurs. The effect, if any, of the small amounts of rhenium on the sag-resistant characteristics of the recrystallized filament is such that filaments embodying the invention are useful in electric lamps and other electrical devices in which the sag-resistance of the filament is of primary importance.

In practice, offsetting appears to be avoided by a grain structure in which there are no grain boundaries striking directly across the cross-section of the body, but rather, essentially all grain boundaries are of a long, tortuous nature and, on the average, lie at low angles to the surface of the body. On the other hand, although grain morphology contributes to sag-resistance, it is not the only factor involved in sag or high temperature creep resistance. The interaction of grain structure with other factors contributing to creep is complex and is best measured by actual sag testing. Filaments made according to the present invention combine a new degree of ductility with sufficient sag and offsetting resistance to be useful in commercial lamps, which is perhaps the most rigorous application of such alloy bodies.

It has been proposed heretofore to improve the ductility of tungsten by the addition thereto of rhenium. As far as applicants are aware, the tungsten to which rhenium alone has been added as an alloying element heretofore has been of the undoped kind, characterized by equiaxed grain growth on recrystallization, which differs from the tungsten used in accordance with the present invention. Applicants have found the use of tungsten doped with grain-growth-promoting additives essential to produce, in the manner disclosed herein, the different alloys having the new, useful and important properties described above.

Filaments embodying the invention are more ductile after recrystallization than are rhenium free filaments. This makes possible the complete processing of a lamp filament, for example, including coiling, annealing, and flashing or aging of the filament before mounting in a lamp to facilitate manufacture of the lamp, to simplify the structure of the lamp and to increase the efficiency of the lamp by eliminating the need for at least some of the light and heat absorbing support wires used heretofore in many types of lamps, as mentioned above. The non-offsetting characteristics of such filaments is not changed by the addition of rhenium metal.

The amount of rhenium in the tungsten based alloy filament effective for attaining the advantages of the invention does not exceed about 7% by weight of the alloy and may be as low as about 0.1% by weight or lower (all percentages given in this specification are by weight unless indicated to be otherwise). The lower limit of rhenium content in alloys of this invention is difficult to establish in terms of numerical percentage. In some lamp applications we have found that 0.1% rhenium is the preferred amount. However, even smaller amounts of rhenium will be equally effective in greatly increasing ductility in a non-sag, non-offsetting elongated body of tungsten alloy doped with aluminum, potassium and sili-

con. Therefore, the lower limit of rhenium content in a tungsten alloy of the invention will be that small but effective amount which imparts a substantial improvement in ductility, as compared with doped, but otherwise unalloyed tungsten. Rhenium contents substantially higher than about 7%, such as about 10%, are not desirable in tungsten alloy lamp filaments, for example, because such filaments develop equiaxed grain structures on recrystallization rather than the elongated grain, non-sag, non-offsetting type of structure. The sag-resistance of the filament is lowered to the extent that the filament is not suitable for use as a light source in electric lamps.

Also, it has been found that sag-resistant tungsten base rhenium alloy filaments in both the fibrous and recrystallized forms of the filaments are of maximum ductility at rhenium contents of about 3% by weight and that the ductility thereof decreases gradually at higher and lower rhenium contents. However, at a rhenium content as high as about 7% and at least as low as about 0.1%, the filament is sufficiently ductile, even after recrystallization, and exhibits sufficient sag resistance to provide the advantages of the invention.

By way of example, tungsten alloys containing rhenium metal in various amounts were prepared by treating blue tungsten oxide powder (approximately W_2O_5) with an aqueous solution of a mixture of potassium silicate and aluminum chloride containing the equivalent of 0.35 gram K_2O , 0.40 gram SiO_2 and 0.10 gram Al_2O_3 per 100 grams of tungsten oxide and then reducing the chemically treated oxide to metallic tungsten by heating in hydrogen in accordance with the teachings of the Pacz patent.

Pure rhenium powder was milled to obtain a fine particle size (Fisher Sub-Sieve Size No. 2, approximately) and then blended with the tungsten powder so prepared. The powder mixtures were pressed at 15 tons per square inch to form ingots of about 600 grams ($\frac{3}{8}$ " x $\frac{3}{8}$ " x 24"). The ingots containing 0 to 7 weight percent rhenium were presintered at 1200° C. in hydrogen, and then sintered by passing an electric current through the ingots in a hydrogen atmosphere. During sintering, the ingots were subjected gradually to 80 percent of their fusion amperage over a period of five minutes; this condition was maintained for 10 minutes, and then the current was raised to 90 percent of fusion amperage and held for 15 minutes prior to cooling. Ingots containing 10 and 20 percent rhenium were presintered in hydrogen at 1200° C., then sintered in vacuum at a pressure of 5×10^{-3} mm. of mercury. Table I shows the hardness and density of the sintered ingots.

TABLE I

Hardness and densities of sintered W-Re alloys

Rhenium, wt., percent	Furnace atmosphere	Hardness Rockwell "A,"* 60 kg. load	Density, g./cc.	Percent theo. density
1.0-----	H ₂ -----	63.5	17.4	89.8
3.0-----	H ₂ -----	61	17.6	90.5
5.0-----	H ₂ -----	59.5	17.1	88.0
7.0-----	H ₂ -----	61	17.2	88.0
10.0-----	Vacuum-----	61	17.9	91.0
20.0-----	do-----	66	18.4	89.8

*Average of 5 readings on cross section of polished section.

Alternatively, the rhenium can be incorporated into the tungsten metal powder as a decomposable compound such as a water solution of ammonium perrhenate. Equivalent effects might be found by incorporating the rhenium either as metal or as a decomposable compound of rhenium in tungsten oxide before reduction to the metal.

A suitable procedure for using a decomposable compound has been found to be to blend into 218-doped and reduced tungsten powder ammonium perrhenate (NH_4ReO_4) dissolved in enough distilled water to form a di-

latent mass (not a free flowing system). The water was then removed by drying the "mud" at about 90° C. and the dried powder then was rolled on a roll mill to dissociate the agglomerates. Hydrogen was infiltrated into the powder which then was heated for about 90 minutes in the hydrogen atmosphere to drive off the ammonia and reduce the perrhenate. Finally, the powder again was rolled and sifted to remove foreign and over-size particles before being pressed into a bar for further processing as described below.

It is now preferred to add rhenium as the metal to produce alloys of 3% rhenium and higher and to use the perrhenate solution addition for alloys of 1% or lower. Rhenium metal powder additions were used to produce the specimens employed to obtain the data presented in Table II below.

Fabrication was by hot swaging the ingots to 0.330" diameter using a furnace temperature of $1625 \pm 25^\circ$ C. At this point, annealing was accomplished by passing 1800 to 1900 amperes through the bars for two minutes in a hydrogen atmosphere. Subsequent swaging to 0.195" diameter was followed by a brief annealing treatment at 2050° C. Swaging from 0.195" to 0.140" was accomplished by using about a 14% reduction per pass and a furnace temperature of 1400° C. After another 2050° C. annealing treatment, swaging was continued to 0.060" diameter. Rods containing 3% or more rhenium were given an extra annealing treatment at 0.105". Drawing from 0.060" to 0.008" diameter was accomplished at gradually diminished temperatures in the range 1050 to 850° C. It was not always possible to follow this schedule precisely; for example, the 10 and 20% rhenium alloys required extra passes.

Tensile tests were performed on specimens of the filaments so prepared. The sag properties of such filaments were measured as well as the electrical resistance thereof. The microstructure of the test specimens also was examined. In certain instances oxidation tests were made and the evaporation of material from the test specimens, under conditions which would show the usefulness of the alloy for electric lamp filaments, was determined. The microhardness of the annealed specimens was determined for several specimens. For purposes of comparison, test specimens of tungsten filaments of the same diameter were prepared in the same manner as described above but with the rhenium metal omitted. The same properties, characteristics and features of these rhenium-free tungsten filaments were determined in the same manner.

The following exemplary data was obtained by these investigations. In Table II the filaments of Al, Si, K doped tungsten free from rhenium are designated as "218," as in the Pacz patent mentioned above; the filaments consisting of 99% of doped tungsten and 1% rhenium are designated as "W1Re," the filaments consisting of 90% of doped tungsten and 10% rhenium are designated as "W10Re" and so forth for the filaments of other compositions. Percentages are in each case weight percentages.

The test for determining the sag of the wire consisted of mounting hairpin or open looped shaped specimens of the wire in a dry hydrogen chamber with the bight and the ends of the loop in a common horizontal plane. The wire specimens were supported only at their ends and were heated twice by passage of electric heater current therethrough of an amperage amounting to 70% of the amperage sufficient to fuse the wire. The initial heating was about one minute to set the structure of the wire. The bight of the loop was supported only during the initial heating. The second heating was about 5 minutes to determine the sag resistance of the unsupported loop of the aged wire. This is known as "sag testing" in the art. The sag is the distance after the second heating between the unsupported bight of the loop and the original common horizontal plane of the loop. This sag test is similar to ASTM Test Procedure F269-52R and differs

principally in the manner of supporting the bight during the initial flashing or recrystallization step.

Oxidation tests were made at 650° C. with a flow of dry air at 600 cc./min. Loss by evaporation was measured for lengths of wire heated to 2500° C. at a pressure of 5 microns for 7 hours. To determine the annealed

ductility of the tungsten-rhenium wires, small lengths (2") were heated in hydrogen for 3 minute periods at temperatures ranging from 1750 to 3000° C. by passing electrical current through the wires. Annealing temperatures were measured by an optical pyrometer with appropriate correction for the emissivity of tungsten. These

TABLE II
Properties of tungsten alloy wire—0.008" diameter

	As drawn	Annealing temperature, ° C. (3 minutes)						
		1750	2000	2240	2500	2750	2850±50	3000±50
218 Tungsten:								
Percent elongation (25° C.)	2.0	0.3	0.5	0.2	0	0	0	
Yield strength, 1000 p.s.i. (25° C.)	326	270	192	190	193	180	163	
Tensile strength, 1000 p.s.i. (25° C.)	400	275	197	193	193	180	163	
Sag, 2850° C., mm.	0.2							
Microstructure	F*	F	Fr*	R*	R	R	R	
El. resist., micro ohm-cm.	6.7							
Evaporation test; 7 hrs., 5μ pressure, 2500° C., percent wgt. loss.	2.18							
Oxidation, percent wgt. increase, 24 hrs. at 650° C. (dry air)	15.4							
Microhardness of annealed wire, 1 kg. load.		544	435	396		391	391	
Alloy W0.1Re:								
Percent elongation (25° C.)	2.0	1	1	5	3	0.5		
Yield strength, 1000 p.s.i. (25° C.)	375	262	262	255	236	220		
Tensile strength, 1000 p.s.i. (25° C.)	465	330	312	322	305	280		
Sag, 2850° C., mm.	0-2							
Microstructure							R	
El. resist., micro ohm-cm.	6.36							
Alloy W.25Re:								
Percent elongation (25° C.)	2.0	3.5	3.5	3	6	6	0.8	
Yield strength, 1000 p.s.i. (25° C.)	363	296	291	277	277	267	179	
Tensile strength, 1000 p.s.i. (25° C.)	427	317	306	292	282	275	179	
Sag, 2850° C., mm.	0-2							
Microstructure	F	F	F	Fr	R	R	R	
El. resist., micro ohm-cm.	6.4							
Oxidation, percent wgt. increase, 24 hrs. at 650° C. (dry air)	14.0							
Alloy W1Re:								
Percent elongation (25° C.)	1.9	2.2	5.8	12.8	16.7	19.3	1.8	1.6
Yield strength, 1000 p.s.i. (25° C.)	312	265	253	240	241	167	122	90
Tensile strength, 1000 p.s.i. (25° C.)	429	273	255	247	249	232	125	93
Sag, 2850° C., mm.	0-2							
Microstructure	F	F	F	F	F	Fr*	R	R
El. resist., micro ohm-cm.	7.7							
Evaporation test, 7 hrs., 5μ pressure, 2500° C.	1.38							
Oxidation, percent wgt. increase, 24 hrs. at 650° C. (dry air)	7.8							
Microhardness of annealed wire, 1 kg. load.		541	524	514	508	490	411	
Alloy W3Re:								
Percent elongation (25° C.)	1.8	9.2	18	20	23	25.7	27.6	7.5
Yield strength, 1000 p.s.i. (25° C.)	390	260	238	219	207	187	155	158
Tensile strength, 1000 p.s.i. (25° C.)	460	266	240	221	212	206	203	202
Sag, 2850° C., mm.	4-5							
Microstructure	F	F	F	F	F	Fr	R	R
El. resist., micro ohm-cm.	9.7							
Oxidation, percent wgt. increase, 24 hrs. at 650° C. (dry air)	3.5							
Microhardness of annealed wire, 1 kg. load.		465	464	414	410	407	377	
Alloy W5Re:								
Percent elongation (25° C.)	1.6	5.1	16.3	19.3	18.0	16.0	23.9	11.7
Yield strength, 1000 p.s.i. (25° C.)	390	271	241	230	215	188	147	135
Tensile strength, 1000 p.s.i. (25° C.)	481	280	245	233	225	217	220	182
Sag, 2850° C., mm.	4-5							
Microstructure	F	F	F	F	F*	Fr*	R*	
El. resist., micro ohm-cm.	12.7							
Oxidation, percent wgt. increase, 24 hrs. at 650° C. (dry air)	2.5							
Microhardness of annealed wire, 1 kg. load.			503			424	389	
Alloy W7Re:								
Percent elongation (25° C.)	2.0	2.5	17.0	17.5	14.5	13.0	9	
Yield strength, 1000 p.s.i. (25° C.)	385	370	223	198	163	154	130	
Tensile strength, 1000 p.s.i. (25° C.)	500	404	250	242	230	220	203	
Sag, 2850° C., mm.	10-16							
Microstructure							R*	
El. resist., micro ohm-cm.	14.0							
Alloy W10Re:								
Percent elongation (25° C.)	1.6	18.5	21.5	21.1	17.6	18.2	7.5	
Yield strength, 1000 p.s.i. (25° C.)	360	260	254	170	154	146	138	
Tensile strength, 1000 p.s.i. (25° C.)	509	267	256	246	246	237	205	
Sag, 2850° C., mm.	30-50							
Microstructure	F	F	Fr*	R	R	R	R	
El. resist., micro ohm-cm.	18.8							
Evaporation test, 7 hrs., 5μ pressure, 2500° C.	1.63							
Oxidation, percent wgt. increase, 24 hrs. at 650° C. (dry air)	1.8							
Microhardness of annealed wire, 1 kg. load.		585	585	585	470		450	
Alloy W20Re:								
Percent elongation (25° C.)	2.2	14.4	6.2	3.5	2.8	2.3	1.0	
Yield strength, 1000 p.s.i. (25° C.)	377	209	184	172	167	162	163	
Tensile strength, 1000 p.s.i. (25° C.)	505	269	207	190	186	178	165	
Sag, 2850° C., mm.	40-60							
Microstructure	F	R	R	R	R	R	R	
Evaporation test, 7 hrs., 5μ pressure, 2500° C.	2.4							
Oxidation, percent wgt. increase, 24 hrs. at 650° C. (dry air)	2.1							
Microhardness of annealed wire, 1 kg. load.		594	538	496	490	467	458	

F* = Microstructure appears fibrous.

r = Microstructure evidence of a minor amount of recrystallization.

R = Microstructure evidence of a major amount of recrystallization.

wires were then tested for strength and ductility in an Instron Tensile machine at a strain rate of 0.1 inch per inch per minute. Another set of wires was annealed at temperatures from 1750–3000° C. for microstructure and hardness studies.

The data tabulated above are average values of two or more identical annealing treatments in the case of each tensile parameter recorded. Sag test data represent a range of values obtained as a result of four tests. The gauge length upon which the "percent elongation" values of Table II were based was one inch and the offset upon which the "yield strength" values given in this table were based was 0.2 percent.

It will be noted from the percent elongation data of Table II that the wires consisting of alloys containing 0.1%, 0.25%, 1%, 3%, 5%, 7%, 10% and 20% rhenium show far greater ductility by several orders of magnitude than 218 tungsten wire after heat treatment at temperatures of 2500° C. and above. The 0.1% and 0.25% rhenium alloys, while having much lower ductility than those of higher rhenium content, are still much more ductile after heat treatment than 218 tungsten, which shows no measurable elongation before fracture after annealing at temperatures of 2500° C. and above. This ductility in alloys containing a small but effective amount of rhenium is what distinguishes the alloys of the invention from prior art sag resistant, non-offsetting filaments, particularly of 218 tungsten. Useful sag-resistance distinguishes filaments of the invention from previously known tungsten-rhenium alloy bodies. The wire consisting of the alloy containing 3% rhenium is particularly useful for incandescent lamp filaments where, in the past, brittleness characteristic of all previous tungsten filaments used commercially for such lamps has been a major cause of failure of lamps by breakage of the filaments as a result of mechanical shock caused by vibration, impact, or both, incident to handling and shipment and during the service of the lamps.

While the sag resistance of the doped wire consisting of the alloys containing 3% rhenium and 5% rhenium is less than the sag resistance of those containing 0.1%, 0.25% and 1% rhenium, the sag resistance thereof is still sufficient to make such wires useful as filaments in electric lamps. As also shown in Table II, wire embodying the invention, both in the recrystallized form, and in the fibrous form, is of maximum ductility at about a 3% rhenium content. The ductility of the wire decreases gradually as the rhenium content increases from 3%, but at 5% the ductility is such that the wire is suitable for lamp filament making purposes. Wires of higher rhenium content, such as a content of 10% rhenium, are not suitable for lamp filaments because the filaments are not sufficiently sag-resistant.

The onset of metallographically observed recrystallization is raised in certain instances as much as 750° C. by the addition of rhenium in amounts of about 3% and about 5%, as shown in Table II. The W1Re, W3Re and W5Re alloys begin to recrystallize at about 2750° C. whereas the W10Re alloy has the same recrystallization onset temperature (2000° C.) as 218 tungsten, and the W20Re alloy has a lower initial recrystallization temperature than 218 tungsten for these three minute treatments.

The results of the sag tests reported in the Table II indicate the creep strength of the wire which determines whether or not the wire is suitable for use in lamps. Sag values in the range of 0 to 7 millimeters, as measured above, are generally satisfactory. Tungsten-rhenium alloys embodying the invention and containing up to approximately 5% rhenium are obviously satisfactory in this respect, but the creep strength of those alloys containing 10% and more of rhenium is too low for use as high temperature lamp filaments. The marginal sag results found for 7% rhenium are considered to be due to the fact that the wire was only partially recrystallized

by the heat treatment. However, the grain structure that was developing was of a non-sag type, and presumably the entire wire would develop this structure on longer heating or heating at a higher temperature. When the wire is treated to develop a non-sag structure, the 7% alloy wire would also have sag properties acceptable for certain lamp use.

Although the time and temperature combinations given in this specification for recrystallization of the various alloys have been found to be generally satisfactory, different time-temperature relations will be found to give equivalent results. This being so, the invention is herein defined by the resulting grain structure and properties. In practice, it may be found when the time of heat treatment is changed from several minutes to a few seconds that an increase in temperature of several hundred degrees is necessary for equivalent results. Much lower temperatures may be satisfactory if the time is increased to several hours.

The results of the oxidation tests show that tungsten is protected from the attack of air at 650° C. by a small rhenium addition. At this temperature a blue oxide replaces the well-known yellow tungsten trioxide and protects the alloy from more rapid oxidation. The increase in room temperature electrical resistance due to rhenium is approximately 1.2 microhm cm. for each percent of rhenium added.

The evaporation tests show that the addition of rhenium in amounts of 10% or lower reduces the amount of material lost at lamp operating temperatures. The amounts of material lost by evaporation are much in excess of what might be expected from simple metallic evaporation. The eroding process in these tests involves oxidation by the residual air under reduced pressure in the test chamber and resembles the well-known water cycle erosion of the filaments in incandescent lamps.

On the basis of the data discussed above, it is apparent that the dilute tungsten-rhenium alloys of the present invention have properties and qualities which are as good or better for use as lamp filaments than the present commercial wire used for this purpose. An examination of the ductility of the wire embodying the present invention shows that this property of the subject wire is highly superior.

For certain applications, filaments made according to the invention have proven to be at least equal in length of life to previously known filaments and show greater resistance to shock and vibration. Also, for electronic tube applications, particularly those requiring sharp bends in filament wires and those in which the filament is normally partially recrystallized, the ductility and adaptability of filaments made according to the invention has proven particularly valuable.

In the drawings accompanying and forming part of this specification, improvements of filament wire of the present invention are shown in which:

FIG. 1 is a graph of ductility in terms of percent elongation at room temperature plotted as a function of the rhenium content showing the effect of the rhenium content on the ductility of some of the rhenium-containing specimens listed in Table II after annealing for three minutes at the temperatures shown on this figure.

FIG. 2 is a graph showing the elongation at room temperature the tungsten of rhenium alloys of the present invention in comparison with that of other alloys and commercial 218 tungsten wire after having been annealed at various temperatures.

FIG. 3 is a reproduction of a photomicrograph which illustrates in longitudinal section at 250 X magnification the typical grain structure of 218 tungsten wire.

FIG. 4 is a similar illustration of the grain structure of a specimen of wire prepared as disclosed above and containing 99.5% doped tungsten and 0.5% rhenium.

FIG. 5 is an illustration similar to FIGS. 3 and 4 of

a specimen of wire similarly prepared and containing 99% doped tungsten and 1% rhenium.

FIG. 6 is an illustration similar to FIGS. 3 to 5 of a specimen of wire similarly prepared and containing 97% doped tungsten and 3% rhenium.

FIG. 7 is an illustration similar to FIGS. 3 to 6 of a specimen of wire containing 97% tungsten and 3% rhenium prepared by well-known powder metallurgy methods but with the chemical treatment or doping of the tungsten oxide with the aqueous solution of a mixture of potassium silicate and aluminum chloride omitted.

FIG. 8 is an illustration similar to FIGS. 3 to 7 of a specimen of wire prepared as the specimens of FIGS. 3 to 6 and containing 90% doped tungsten and 10% rhenium.

FIG. 9 is a bar graph representing the results of sag tests on wires of various alloy compositions including 0% rhenium which is the 218 tungsten described above.

The wire specimens of FIGS. 3, 4 and 6 to 8 were of 0.008 inch diameter, whereas the specimen of FIG. 5 had a diameter of 0.0065 inch. All the wire specimens illustrated in FIGS. 3 to 8 were annealed at 2850° C. for three minutes to recrystallize the specimens to the grain structures shown in these figures.

As shown in the Table II and in the graph of FIG. 1, the alloy containing 97% doped tungsten and 3% rhenium has the best ductility at room temperature of all the specimens tested after annealing at temperatures of 2500° C., 2750° C. and 2850° C. These annealing temperatures cover the operating temperature range of most incandescent lamp filaments.

The elongation data included in Table II and illustrated graphically in FIGS. 1 and 2 shows the superior ductility of the tungsten rhenium alloys examined in comparison with 218 tungsten. The three "non-sag" alloys represented in FIGS. 1 and 2, W1Re, W3Re, and W5Re, all appear to have similar temperature elongation relations, with elongation increasing with annealing temperature to the point at which recrystallization is nearly complete and decreasing sharply with complete recrystallization. However, even after recrystallization, the remaining ductility is much greater than that of non-sag tungsten filament wire previously known, as noted above. As can be seen from Table II, the 0.1 and 0.25% rhenium alloys behave similarly.

The improvement in ductility of the dilute tungsten-rhenium alloys of the present invention is apparent from the fact that after specimens of such alloys were tested for sag at 2850° C. as described above, the test specimens could be bent, twisted and even tied into knots without breaking.

Commercial lamp wire having non-sag characteristics is characteristically extremely brittle after being submitted to the sag test.

FIGS. 4 to 6 of the drawings show that the grain structure characteristic of non-sag lamp wire, designated as 218 in the Table II and shown in FIG. 3 as prior art, is retained in the tungsten-rhenium alloys of this invention. This grain structure is characterized by the presence of large elongated grains 1, elongated in the direction of working of the wire, the boundaries of which make, on the average, relatively small angles with respect to the longitudinal axis of the wire. In FIG. 5, an elongated crystal 1 occupies the full diameter of the wire.

The fine grained structure of the 90% chemically treated or doped tungsten, 10% rhenium alloy wire shown in FIG. 8 is not characteristic of the 218 tungsten wire and, as shown in the table, wire of this alloy does not have the non-sag qualities required for satisfactory lamp filament wire. The fine-grained structure shown in FIG. 8 is typical of recrystallized tungsten-rhenium alloys containing 10 percent or more rhenium when the tungsten powder used to form the alloys has been produced from either undoped tungsten oxide or tungsten oxide doped with materials promoting exaggerated grain growth.

As a result of the investigations leading to the present invention, it was found that 3% rhenium alloyed with 97% tungsten produced from tungsten oxide, which has not been chemically treated or doped with the usual exaggerated grain growth promoting materials mentioned above, formed wire which was not ductile after recrystallization at temperatures of 2850° C. On the contrary, the specimen wires were exceedingly brittle and fractured when bent even slightly. In contrast, the wire specimens consisting of 97% doped tungsten and 3% rhenium, after being recrystallized by annealing at a temperature of 2850° C. could be bent back on themselves without fracture.

Further, the 97% undoped tungsten, 3% rhenium alloy does not have the sag resistant qualities necessary for lamp filament wire, but on the contrary the sag resistance thereof was no better than that of wire consisting of undoped tungsten alone. The grain structure of the 97% undoped tungsten, 3% rhenium alloy was different from the grain structure characteristic of lamp wire having satisfactory sag resistance qualities and was fine grained, as shown in FIG. 7 of the drawings.

The reason for the great difference in ductility after recrystallization of the two alloys containing 3% rhenium is not known. Inasmuch as the alloys are of different grain structure it may be that the effect of the rhenium on ductility occurs at grain boundaries and that, due to the greater area of such boundaries in a fine grain structure than in a coarse grain structure, more rhenium is required for producing ductility in the former than in the latter structure. It is not known whether or not this is a true explanation of the difference of the effect of the rhenium content on the alloys of different grain structure, but the difference in the effect has been established by the procedures described above.

The sag test results represented in FIG. 9 are illustrative of the upper limit of the rhenium in alloys of the invention. The tests were run for five minutes at 2850±50° C. after flashing to develop the grain structure of the wire. The range of data points obtained on four specimens of each composition is shown by lines for 0% (corresponding to 218 wire), 0.1%, 2.25% and 1.0% rhenium alloys, balance doped tungsten, and by bars for the 3.0%, 5%, 7%, 10.0% and 20.0% alloys. On the bars, the open areas indicate the ranges of values obtained, while the cross-hatched areas contained no data points. The figures in parentheses at the top of each bar or line state the ranges of values represented by the bar or line.

It is apparent from the graph that the sag properties of 218 tungsten and the 0.1%, 0.25%, 1.0%, 3.0% and 5.0% alloys are closely related, while the 10% and 20% alloys are of a different kind, having far less resistance to sag. The values obtained for the 7.0% alloy are intermediate but closer to those of the lower alloy group than the higher alloy group. As explained above, the 7% alloy data was obtained on partially recrystallized material, and fully recrystallized 7% alloy wire will have better sag resistance than is shown in Table II and FIG. 9.

Alloys of the invention and filaments made therefrom should not contain extraneous material in significant amounts such as to detract from the advantageous properties attained by this invention. For example, the addition of vanadium to an alloy of tungsten-rhenium, as disclosed in Laise Patent 2,202,108, deleteriously affects important properties of lamp filaments made from such alloy, such as the ductility and sag resistance of such filaments, and contributes to premature blackening of lamp envelopes with consequent loss of luminous efficiency. Again, any significant quantity of molybdenum, even in amounts in the range of 1% as disclosed in Hensel Patent 2,157,935, results in an alloy which has been found to be highly volatile at lamp operating temperatures and leads to bulb blackening, seriously lowering light output or contaminating the electron emissive surfaces in

various types of electronic tubes. The increased ductility, the resistance to sag, and the lack of volatility of the alloy of the invention is attained when rhenium, within the specified range of composition, is the alloying element with doped tungsten. As far as we know, these desirable properties are not attained, or are significantly destroyed, when other alloying elements such as the molybdenum and vanadium metals previously mentioned are present in doped tungsten-rhenium alloys of the invention. (Needless to say, any alloy body not having the type of grain structure of the invention, at least to a substantial extent, would not serve the purposes of the invention.)

The diameter of the wire of the invention may be reduced, and the wire may be formed into coils and coiled coils after recrystallization by conventional methods and means for use as incandescible filaments or heaters in commercial incandescent lamps of various wattage and voltage sizes and in electronic tubes. The aging of the wire may be done either before or after forming the wire into the desired coiled configurations and either before or after mounting the wire in the lamp. The wire may also be used as current inleads and supports for lamp filaments and as heaters and cathodes and other components of electronic tubes. Thermocouples for making ultra high temperature measurements advantageously may incorporate the wire which is ductile after recrystallization.

Although the present invention has been described in relation to metals consolidated by powder methods, it should be manifest that the principles of the invention could be applied to alloys consolidated by arc-melting or other methods. Likewise, the alloy constituents could be initially combined by powder processes, arc melting, or otherwise. Elongated alloy bodies as described above, which are characterized by non-sag properties and grain structure and by significant room temperature ductility, are part of the invention apart from the method of consolidation.

While the best mode contemplated for carrying out the invention has been described above, it will be understood, of course, that changes may be made by those skilled in the art without departure from the spirit and scope of the invention as defined in the appended claims.

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

1. The method of producing a tungsten-rhenium alloy body consisting essentially of from a small but effective amount to increase ductility to about 7% rhenium by weight, minute quantities of grain-growth-promoting material, and balance tungsten, which comprises treating tungsten oxide with exaggerated-grain-growth-promoting material, reducing the treated tungsten oxide to tungsten metal powder in a non-oxidizing atmosphere, forming a mixture of at least one of the group consisting of rhenium metal powder and a rhenium compound decomposable to rhenium metal and volatile matter when heated under nonoxidizing conditions to elevated temperatures sufficient to sinter the tungsten powder with one of the group consisting of said treated tungsten oxide powder before reduction and said tungsten metal powder after reduction, with the rhenium expressed as metal being an amount such that the rhenium content of the produced tungsten-rhenium alloy is from a small but effective amount to increase ductility to about 7% by weight of the alloy, compacting the powder to form an ingot, sintering the ingot in a non-oxidizing environment, and mechanically working the ingot into an elongated alloy body, whereby the alloy body, when heated to a temperature and for a time sufficient to cause substantial recrystallization, is ductile and sag-resistant and shows crystal grains elongated in the direction of working of the body.

2. The method of claim 1 in which the exaggerated-grain-growth-promoting material is composed of potassium, silicon and aluminum compounds.

3. The method of producing a tungsten-rhenium alloy body consisting essentially of from a small but effective amount to increase ductility to about 7% rhenium by weight, and minute quantities of grain-growth-promoting material, balance tungsten, which comprises treating blue tungsten oxide with an exaggerated-grain-growth-promoting aqueous solution of a mixture of potassium silicate and aluminum chloride containing the equivalent of about 0.35 gram K_2O , 0.40 gram SiO_2 and 0.10 gram Al_2O_3 per 100 grams of tungsten oxide, reducing the treated oxide to tungsten metal powder by heating in hydrogen, mixing pure rhenium metal powder with the tungsten metal powder in such amount that the rhenium content of the produced tungsten-rhenium alloy body is from a small but effective amount to increase ductility to about 7% by weight of the body, compacting the powder mixture to form an ingot, sintering the ingot in a nonoxidizing environment, and mechanically working the ingot into an elongated alloy body, whereby the alloy body, when heated to a temperature and for a time sufficient to cause substantial recrystallization, is ductile and sag-resistant and shows grains elongated in the direction of working of the body.

4. An incandescible filament suitable for lamp use at temperatures in excess of $2500^\circ C.$ consisting of an alloy body consisting essentially of from about 5% to about 0.1% by weight of rhenium, grain controlling additives, and the balance tungsten, said filament, when heated to a temperature sufficient to cause substantial recrystallization, being ductile and sag-resistant and showing elongated crystal grains extending longitudinally of the filament.

5. A filament as defined in claim 4 consisting essentially of about 3% by weight of rhenium, grain controlling additives, and the balance tungsten.

6. An alloy body consisting essentially of from a small but effective amount to increase ductility to about 7% by weight of rhenium, grain-growth-promoting additives, and the balance tungsten, said alloy body, when elongated and heated to a temperature and for a time sufficient to cause substantial recrystallization, being ductile and sag-resistant and showing elongated crystal grains, extending in a common direction.

7. An alloy body as defined in claim 6 consisting essentially of from about 0.1 to about 5% by weight of rhenium, grain-growth-promoting additives and the balance tungsten.

8. An electric lamp including an incandescible filament consisting of the alloy body defined in claim 6.

9. An electrical device including a heater element comprising the alloy body defined in claim 6.

10. A substantially recrystallized, elongated alloy body having a grain structure comprising elongated grains with irregular grain boundaries forming, on the average, small angles with the surface of the body, said alloy body consisting essentially of from a small but effective amount to increase ductility to about 7% by weight of rhenium, together with minute quantities of grain-growth-promoting additives effective for producing said grain structure, and the balance tungsten, said alloy body having significantly greater room temperature ductility than recrystallized, doped, but otherwise essentially pure tungsten and significantly greater elevated temperature creep resistance than tungsten-rhenium alloy bodies having the same rhenium content and characterized by an equiaxed grain structure.

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