Oct. 11, 1966 H. J. EHRINGER 3,278,281

THORIATED TUNGSTEN FILAMENT OR WIRE AND METHOD OF MAKING SAME

Filed Sept. 13, 1957 4 Sheets-Sheet 1

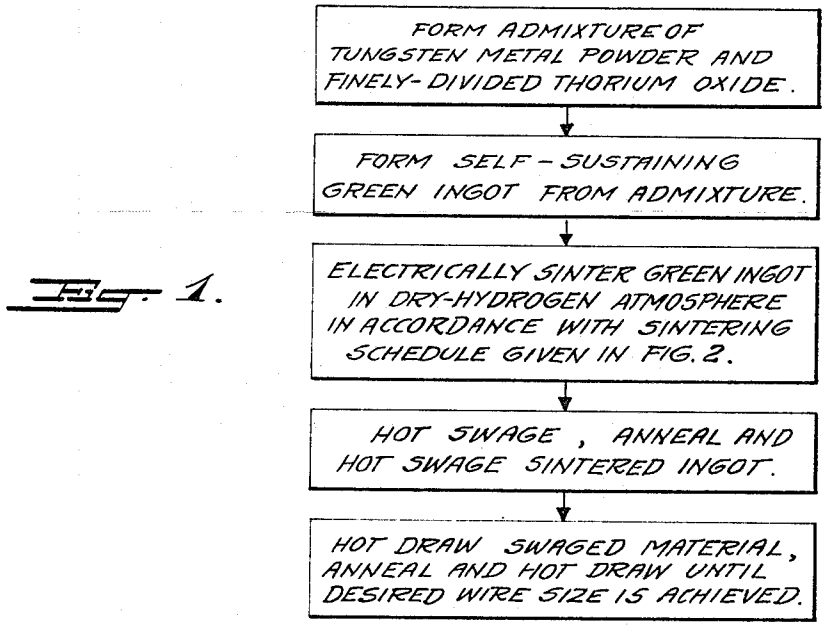

Fig. 1.

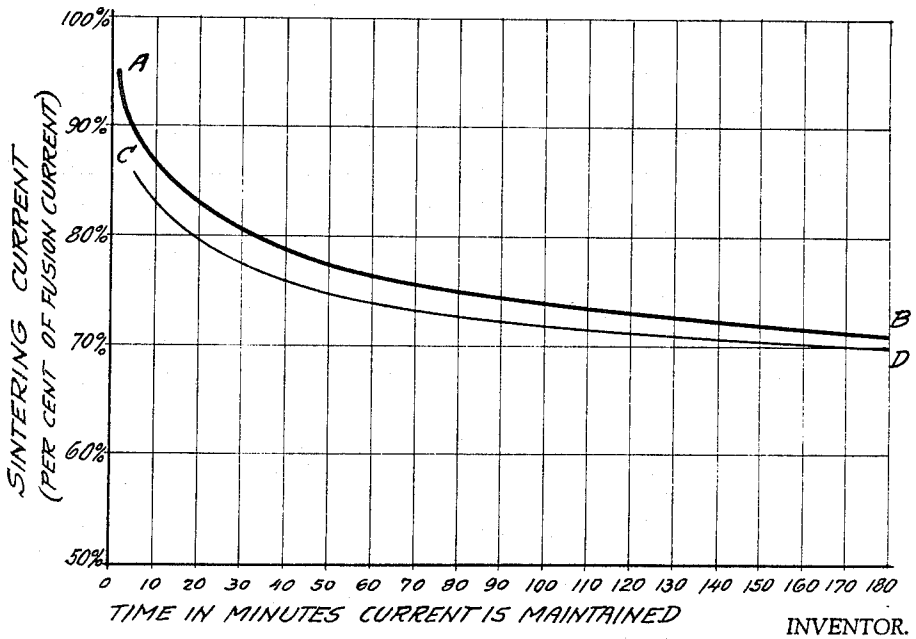

Fig. 2.

INVENTOR.
HERMANN J. EHRINGER.
BY W. D. Palmer
ATTORNEY.

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Fig. 3.

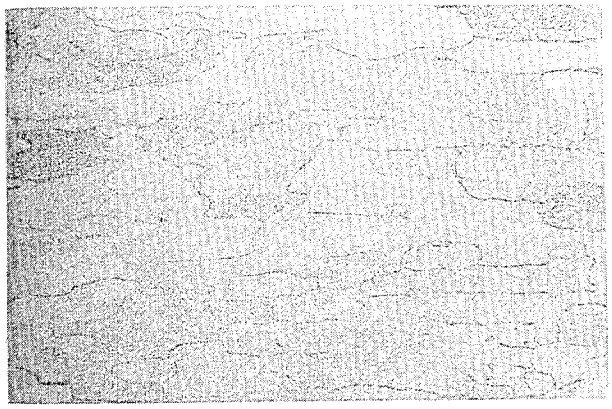


Fig. 4.

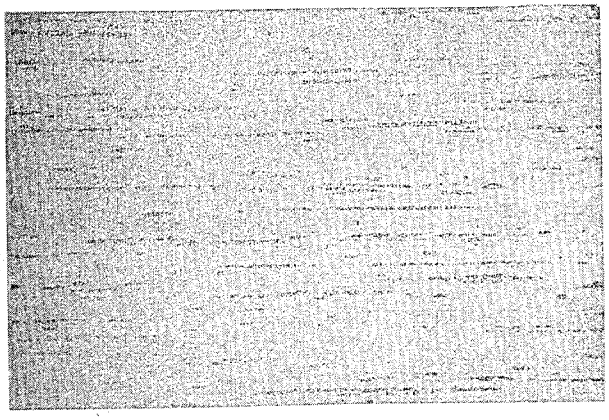
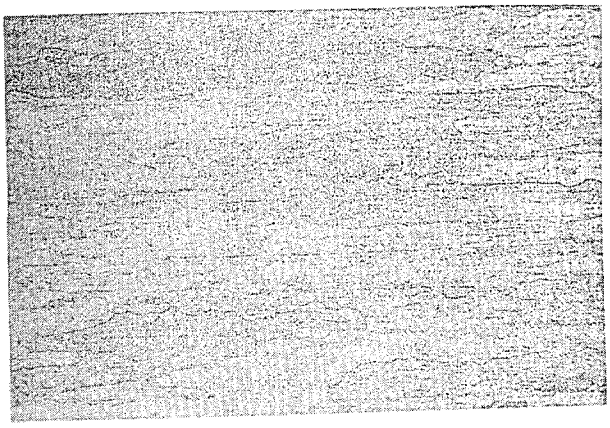


Fig. 5.



INVENTOR.
HERMANN J. EHRINGER
BY
W. D. Palmer
ATTORNEY.

THORIATED TUNGSTEN FILAMENT OR WIRE AND METHOD OF MAKING SAME

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Fig. 6.

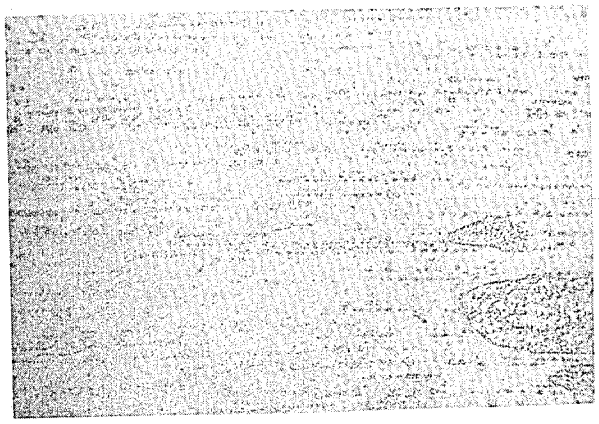


Fig. 7.

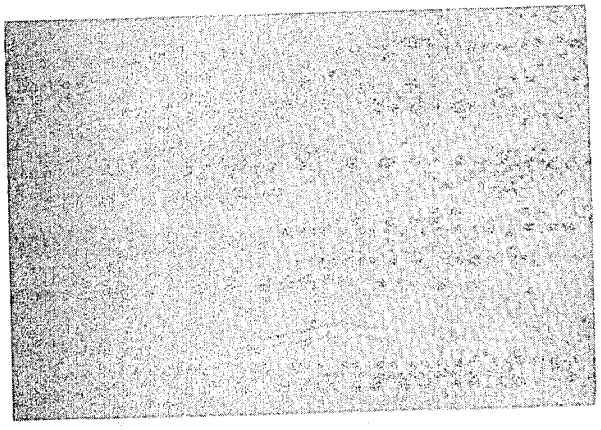
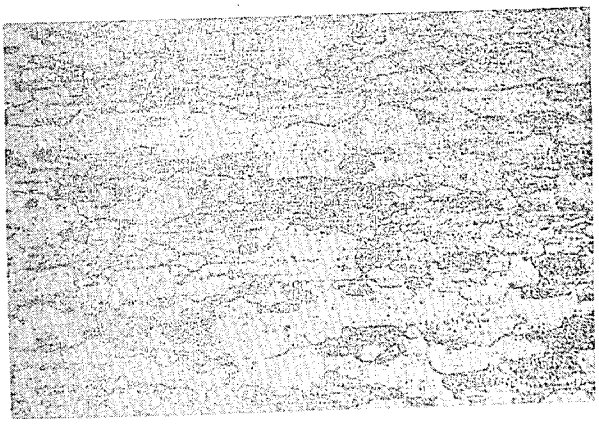


Fig. 8.



INVENTOR.
HERMANN J. EHRINGER
BY
W. D. Palmer
ATTORNEY

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Fig. 9.

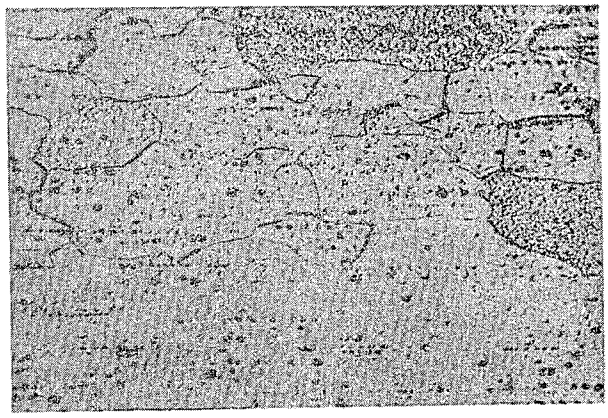
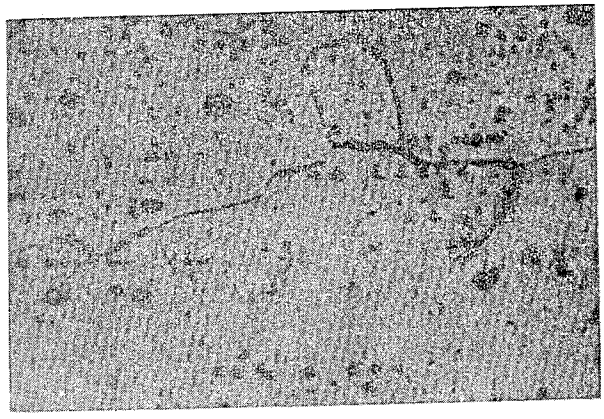


Fig. 10.



INVENTOR.
HERMANN J. EHRINGER
BY
W. D. Palmer
ATTORNEY

United States Patent Office

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THORIATED TUNGSTEN FILAMENT OR WIRE AND METHOD OF MAKING SAME

Hermann J. Ehringer, West Orange, N.J., assignor to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

Filed Sept. 13, 1957, Ser. No. 683,809
19 Claims. (Cl. 29—182.5)

This application is a continuation-in-part of my copending application Serial No. 683,361, filed September 11, 1957, now abandoned, and owned by the assignee of the present application.

This invention relates to filament wire and filaments for incandescent lamps and to methods for making such wire and, more particularly, to a shock-resistant, vibration-resistant and non-sag filament wire and filaments suitable for use in incandescent lamps and to a method for making such filament wire.

The impact resistance of the usual incandescent lamp filaments is very poor when the unenergized filaments are subjected to shock and vibration. Even when energized, the impact resistance of such filaments under conditions of shock and vibration is quite poor. In the early development of tungsten filaments for incandescent lamps, the filaments broke easily and sagged greatly after initial energization, which resulted in very poor performance for the incandescent lamps. Thereafter, so-called doping impurities were added to the tungsten filaments, which doping impurities improved the filament strength and directed the tungsten grain growth within the energized filaments, in order to form what are known as interlocking crystals or grains. These doping impurities drastically improved the performance of incandescent lamps and revolutionized the industry. One of the first doping additives which was utilized was thorium oxide and this doping additive served to strengthen the filament against shock and vibration, although the thoria-doped wire had very poor non-sag characteristics.

The use of thoria as a doping additive to a tungsten filament was superseded by later-developed doping additives, since these gave much better non-sag characteristics. In the present practices potassium, alumina, and silica are added as potassium chloride, potassium silicate and aluminum chloride, for example, and are used as doping additives. These materials are normally added to the tungstic oxide or to acid, before the tungsten is sintered as an ingot and thereafter swaged and drawn into wire. As an example, residual doping constituents after reduction may comprise 0.3% by weight potassium, 0.02% by weight alumina, and 0.4% by weight silica. These doping constituents may vary both in amount and formulation, but the foregoing are representative of the present practices.

The foregoing potassium, alumina, and silica-doped wire possesses excellent non-sag characteristics, but the impact resistance of such wire when subjected to vibration or shock is comparatively poor. Because of its excellent non-sag characteristics, however, it is normally used in applications where non-sag, vibration-resistant and shock-resistant characteristics are required. This has resulted in extremely poor life in such applications as dashboard and trunk lights for automobiles and toy electric trains, for example, where the lamps are subjected to considerable shock and vibration.

When an incandescent lamp filament coil sags the longitudinal coil dimension increases. This alters the lumen output of the lamp and usually causes turns of the filament coil to short out, with resultant failure. The term non-sag is normally used in the art to describe a filament coil which has sufficient resistance to coil elongation to cause the lumen output of the lamp to be relatively uniform and to prevent turns of the filament coil from shorting out to cause premature failure. This is the meaning given to the term "non-sag" as used herein.

In order to avoid and overcome the foregoing and other difficulties of and objections to the practices of the prior art, it is the general object of this invention to provide a shock resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps.

It is a further object to provide a shock-resistant, vibration-resistant and non-sag filament suitable for use in incandescent lamps.

It is another object to provide a shock-resistant, vibration-resistant and non-sag filament suitable for use in incandescent lamps, wherein the filament comprises a plurality of interlocking crystals or grains which are maintained as such.

It is a still further object to provide a process for forming shock-resistant, vibration-resistant, and non-sag filament wire suitable for use in incandescent lamps.

It is still another object to provide permissible and preferred process steps and conditions for forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps.

The aforesaid objects of the invention, and other objects which will become apparent as the description proceeds, are achieved by providing a filament and filament wire wherein the filament and wire have included therein a plurality of minute segregations which comprise thorium oxide, substantially all of which segregations are aligned in a plurality of discontinuous groupings which are longitudinally disposed throughout the wire, that is, disposed in the direction of working. When the filament is energized and recrystallizes, the crystals are elongated and interlocking and follow the disposition of the segregation groupings within the wire. These interlocking crystals are maintained as such by the aligned segregation groupings. There are also provided process steps for fabricating the wire, which process steps include a current-time sintering schedule which is necessary to the production of the instant filament wire. There are also provided permissible and preferred ranges for the doping material as well as permissible and preferred variations in the process for forming the wire.

For a better understanding of the invention, reference should be had to the accompanying drawings wherein:

FIG. 1 is a flow diagram illustrating the process steps involved in preparing the improved wire;

FIG. 2 is a graph of sintering current expressed as a percent of ingot fusion current vs. time, which curve sets forth the percent of fusion current-time relationship which is necessary to produce the instant wire;

FIG. 3 is a photomicrograph showing an etched section of the prior-art potassium, alumina and silica-doped wire, after recrystallization;

FIG. 4 is a photomicrograph of an etched section of the instant wire before recrystallization;

FIG. 5 is a photomicrograph of an etched section of the instant wire, after recrystallization, illustrating the interlocking crystal structure;

FIG. 6 is a photomicrograph of an etched section of the instant wire as shown in FIG. 5, but taken at a higher magnification;

FIG. 7 is a photomicrograph of the same section of the instant wire as shown in FIG. 6, but taken at a still-higher magnification;

FIG. 8 is a photomicrograph of an etched section of thoria-doped wire, after recrystallization, wherein the permissible ingot sintering current-time relationships as set forth in FIG. 2 have been exceeded;

FIG. 9 is a photomicrograph of an etched section of thoria-doped wire as shown in FIG. 8, but taken at a higher magnification;

FIG. 10 is a photomicrograph of the same section of thoria-doped wire as shown in FIG. 9, but taken at a still-higher magnification.

In accordance with the general process steps as illustrated in FIG. 1, tungsten ore is digested and reacted to form ammonium paratungstate. This procedure is well known and includes as a final step reacting ammonium tungstate and hydrochloric acid to produce ammonium paratungstate. To the ammonium paratungstate is added thorium nitrate in the form of a water solution in concentration of 0.83 gram C.P. grade thorium nitrate in ten cc. of water, for example. The thorium nitrate and ammonium paratungstate are thoroughly admixed, as by stirring, to form a homogeneous paste. Thereafter the paste is dried and is fired in air at a temperature at about 1000° C. for about two hours, for example, or until the ammonium paratungstate is converted to tungstic oxide (WO_3) and the thorium nitrate is converted to ThO_2. The firing temperature of 1000° C. is given only by way of example and may be varied considerably. The amount of thorium nitrate in the initial admixture should be such that the percent by weight of thorium, expressed as the oxide, with respect to the tungsten, expressed as metal, is from ¼% to 4% and preferably from ¾% to 1½%. As a specific example, the percent by weight of thorium, expressed as the oxide, is 1% of the weight of the tungsten metal in the admixture.

The admixed thorium oxide and tungstic oxide are then fired in a reducing atmosphere such as dry hydrogen. As a specific example, a boat containing 100 grams of the admixture is fired in the dry-hydrogen atmosphere (maintaining a flow of fifty cubic feet per hour), first at a temperature of about 640° C. for sixty minutes, then at a temperature of about 840° C. for sixty minutes and finally at a temperature of about 1000° C. for another sixty minutes. This reducing schedule is dependent on the batch size and may be varied considerably. However, the foregoing schedule is very satisfactory. This will reduce the tungstic oxide to finely-divided metallic tungsten and the thorium oxide will remain as such. The finely-divided admixture of thorium oxide and tungsten metal powder are then formed into pressed green ingots. As a specific example, 2050 grams of the admixture are pressed into an ingot having dimensions of 0.725 inch by 0.655 inch by 24 inches and the pressure used to form the ingot is 17 tons per square inch. While the resulting pressed green ingot has sufficient strength to facilitate its being handled, where an electrical sintering technique is utilized it is highly desirable to pre-sinter the ingot in order to render it more self-sustaining in nature so that it may readily be clamped between electrodes during electrical sintering. As a specific example, the pressed green ingot is pre-sintered in a dry-hydrogen atmosphere at a temperature of about 1000° C. for about 20 minutes, for example, using an electrical furnace. This will impart to the green ingot a sufficient amount of pre-sintering in order to render the ingot quite self-sustaining. This pre-sintering schedule may be varied considerably.

The self-sustaining green ingot is then placed in a vertical position in an electrical sintering bottle, wherein the top end portion of the ingot is clamped between heavy molybdenum electrodes and a tungsten contact clamp connects to the bottom portion of the ingot and is suspended in a mercury pool to facilitate electrical contact. Electrical sintering is normally effected in a dry-hydrogen atmosphere in a double-walled copper bottle which preferably is water cooled, such sintering bottles being well known. With an ingot of the aforementioned dimensions, a flow of hydrogen through the sintering bottle of 100 cubic feet per hour has been found to be satisfactory.

The formation of the instant shock-resistant, vibration-resistant and non-sag tungsten wire has been found to be dependent upon a temperature-time relationship, as will be explained in detail hereinafter. In addition, for the specific ingot swaging schedules as given hereinafter, it has been found necessary to sinter the ingot at a sufficient current and for a sufficient time in order to impart to the ingot a sufficient density to enable it to be mechanically reduced in size (i.e., swaged and later drawn) without fracturing. For the specific ingot dimensions and swaging schedules considered herein, a sintered ingot density of at least about 16.4 is desired and preferably the density of the sintered ingot is at least about 17.1. Normally the higher the ingot sintering current and the longer such sintering current is held, the greater the density of the resulting ingot. Ingot densities greater than those usually obtained (e.g., 17.1–17.8) normally are not a factor with regard to enabling a sintered ingot to be reduced in size without fracturing. By altering the swaging schedules to increase the temperatures at which the sintered ingot is swaged, the lower limit for the permissible ingot density may be extended, and vice-versa, if the swaging temperatures for the ingot are decreased, the ingot desirably is sintered so as to have at least the preferred minimum density. As a specific example, a maximum ingot sintering current of about 72% of the ingot fusion current, when maintained for about five minutes, normally will not produce an ingot of sufficient density to enable it to be swaged without fracturing, unless special swaging precautions are taken. If the ingot sintering time at this maximum ingot sintering current is extended to about sixty minutes, the ingot normally can be swaged, according to the schedule described hereinafter, without fracturing. Thus it can be seen that the selection of the minimum temperature-time relationships necessary to enable the ingot to be mechanically reduced in size without fracture are a matter of choice and design and are dependent on ingot dimensions and swaging schedules as well as ingot sintering schedules. This requirement has existed with tungsten wire as manufactured in accordance with the teachings of the prior art as well as the instant wire.

In the curve A–B in FIG. 2 are plotted R.M.S. current-time relationships for the sintering schedule for producing the instant wire, wherein the maximum ingot sintering current (expressed as a percent of ingot fusion current) is plotted vs. time such current is maintained. Fusion or melting current for the specific ingot described herein is 6700 amperes (60 c.p.s.). If the maximum sintering current is maintained for a sufficient time to cause the plot of ingot sintering current vs. time to fall on or above the curve A–B in FIG. 2, the resulting sintered ingot cannot be formed into a filament which combines all the properties of shock-resistance, vibration-resistance and non-sag characteristics. If the plot of ingot sintering current vs. time falls below the curve A–B in FIG. 2, the resulting ingot can be formed into shock-resistant, vibration-resistant and non-sag wire suitable for use in incandescent lamps, provided of course that the ingot has sufficient density to enable it to be reduced in size without fracturing. Preferably the plot of ingot sintering current vs. time falls below curve C–D in FIG. 2 in order to produce the best-possible filament. Manufacturing practices where large production is involved must provide large tolerances in order to keep costs as low as possible. The curve C–D in FIG. 2 takes into account factory tolerances and in the usual factory practices, the curve C–D will be used as a guide in the sintering schedule for producing the instant wire. In addition, the formation of the instant wire involves a temperature-time relationship during sintering, as explained hereinafter, and it is desired to keep this temperature-time relationship as low as possible commensurate with providing a sufficient density for the sintered ingot to enable it to be reduced in size without fracturing.

The curves A–B and C–D are expressible by formulas as follows: sintering current

$$(\text{curve A–B}) = 70 + (14.8)(e^{-t/67}) + (11.2)(e^{-t/11.5})$$

where sintering current is expressed as a percent of the ingot fusion current and "t" in minutes is at least 2; sintering current

$$(\text{curve C–D}) = 69.5 + (8.3)(e^{-t/80}) + (10.4)(e^{-t/18.5})$$

where sintering current is expressed as a percent of the ingot fusion current and "t" in minutes is at least 5. Thus to produce the instant wire, the green ingot is electrically sintered at such sintering current and for such time that the resulting sintered ingot may be reduced in size without fracturing and so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time in minutes falls below the curves represented by the foregoing formulas, with the choice of curves which are represented by these formulas dependent on whether the permissible or preferred sintering schedule is to be followed.

As a specific example for sintering an ingot as specified hereinbefore, in accordance with the instant process, following is a suitable sintering schedule:

Sintering current, R.M.S. amperes (60 c.p.s.):	Time current is held minutes
500	1
800	3
1000	2
1400	5
1800	4
2200	3
2600	3
3000	2
3400	2
3800	2
4200	2
4400	10
4800	½
5200	½
5400=80.7% of fusion amps	10

The maximum sintering current is normally held for a somewhat extended period and it is this maximum sintering current which is effective in causing the resulting wire to have the desired characteristics. In the above-detailed sintering schedule, the sintering currents are increased gradually. This is primarily because some impurities are present in the tungsten and it is desirable to volatilize all impurities as well as to convert any remaining tungstic oxide to metallic tungsten before increasing the sintering current to its maximum. If special precautions were taken to purify to a high degree the constituents of the pressed and unsintered ingot, the initial sintering steps, wherein the ingot sintering current is gradually increased, could be shortened considerably and the ingot sintering current raised to a maximum in a more rapid fashion. It is more economical, however, to eliminate impurities by a sintering schedule such as the foregoing.

The curves A–B and C–D in FIG. 2 thus define the limits for the permissible and the preferred ingot sintering currents and the time which such sintering currents may be maintained. As a specific example of an unsuitable sintering schedule for producing the instant wire, a maximum ingot sintering current of 87%–90% of ingot fusion current, when maintained for a period of twenty-five minutes, will describe a point which falls above the curve A–B in FIG. 2. A maximum sintering current of 80% of the ingot fusion current, when maintained for a period of twenty minutes constitutes a permissible sintering schedule, although it is preferable to hold this maximum ingot sintering current of 80% of the ingot fusion current for a period of about 10 minutes, for example.

After the ingot has been sintered for the prescribed time at the indicated currents, it is cooled within the sintering bottle while maintaining the stream of dry hydrogen thereover. Approximately 5% of the length dimension is removed from each end of the cooled and sintered ingot, since the sintering of these portions will be uneven due to the contact electrodes, such a procedure being standard sintering practice. The resulting sintered ingot is then heated to approximately 1600° C.–1650° C. in a non-oxidizing atmosphere such as hydrogen and swaged through three swaging dies, using conventional swaging equipment and conventional swaging practices. This will produce a partially-swaged ingot of generally-circular cross-sectional area, having a diameter of approximately 0.467 inch. The partially-swaged ingot is then annealed to relieve strains and annealing may be accomplished by passing a current of 2600 amps. therethrough for a period of two minutes, while maintaining the partially-swaged ingot in a dry-hydrogen atmosphere. Thereafter the ingot is reheated to approximately 1350–1400° C. and is swaged through two swaging dies to a diameter of about 0.337 inch. The partially-swaged ingot is then reheated to about 1900° C. in a non-oxidizing atmosphere such as hydrogen for about three minutes, in order to relieve strains, and it is thereafter heated to about 1300° C. and swaged to a cross-sectional diameter 0.186 inch. The partially-swaged ingot is then annealed to a temperature of 1950° C. in a non-oxidizing atmosphere such as hydrogen for about one and one-half minutes, reheated to about 1300° C. and reswaged to a cross-sectional diameter of about 0.083 inch.

The foregoing swaging procedures result in a greatly-elongated bar and after the diameter of 0.083 inch is achieved, further reduction in diameter is achieved through hot-drawing, using conventional drawing equipment and conventional drawing practices. In the hot-drawing procedure, the elongated material is heated to approximately 800 to 900° C. and is reduced approximately 12% in diameter on each pass through a die. After approximately every fifth pass through the drawing dies, the drawn material is annealed to relieve strains and an annealing temperature of about 1700° C. in a non-oxidizing atmosphere such as hydrogen for about ten seconds is suitable. The drawing procedures are continued until the desired wire diameter is achieved, which as a specific example is 1.23 mils. It should be understood that the foregoing swaging-annealing-swaging-drawing-annealing-drawing procedures are only given in detail by way of specific example and may be varied considerably to produce substantially the same end effect. Also, while the foregoing swaging and later drawing schedules for the instant wire have all been of a mechanical nature, it should be understood that the final reductions in wire size could be effected by other than mechanical means, such as the electrolytic reduction process described in Patent No. 2,784,154 to Korbelak et al.

After the wire has been drawn to size, it is formed into filament coils by well-known techniques, and then incorporated into lamps. Such filament coils normally have a generally-helical configuration and in some cases the helical coils are again coiled to form a coiled-coil, such practices being usual in the art.

In FIG. 3 is shown a photomicrograph of a recrystallized and etched section of the best-available wire for applications requiring shock-resistant, vibration-resistant, and non-sag characteristics, which wire is potassium, alumina and silica-doped, as noted hereinbefore. When lamp filaments of such wire are initially energized, the tungsten comprising the filament recrystallizes and the doping additives cause the tungsten crystals to have either a single crystal or an interlocking structure, or both. These crystal structures are subject to failure under shock and vibration, although they display excellent non-sag characteristics.

In FIG. 4 is shown a photomicrograph (1000×) of an etched section of the instant wire before recrystallization. The photomicrograph of the etched wire discloses a plurality of minute segregations which are distributed within the wire and substantially all of these segregations are aligned in a plurality of discontinuous groupings which are longitudinally disposed throughout the wire. The

elongated crystal or grain boundaries appear as a series of continuous lines disposed in the direction of working. On recrystallization these grains will grow as shown in FIG. 5.

In FIG. 5 is shown a photomicrograph (250×) of an etched section of filament wire manufactured in accordance with the instant process and energized at its normal operating temperature for a sufficient time to cause recrystallization. This photomicrograph was taken at too low a magnification to show the general distribution of the minute segregations which are included within the wire. It does illustrate, however, the interlocking crystal structure which is obtained after the instant wire has been recrystallized and this photomicrograph is to be contrasted with the photomicrograph of FIG. 8.

The term "interlocking crystal structure" is generally used in the tungsten filament art to describe crystals or grains comprising the filament which are elongated in the direction of working, with the end portions of the grains overlapping. This inhibits slippage at the grain boundaries since the overlapping structure "locks" the grains with respect to one another. It is this generally-accepted meaning of the term "interlocking crystal structure" which is used herein to describe the crystal structure of the instant wire after recrystallization. The term "recrystallization" as generally used in the art, and as used herein, refers to the appearance of discrete, nearly-perfect crystalline grains which are formed upon initial energization of the filament at its normal operating temperature. Such recrystallization may be demonstrated with a photomicrograph technique, as in the instant case.

In FIG. 6 is shown a photomicrograph (1000×) of an etched filament section manufactured in accordance with the instant process and energized at normal operating temperature for a sufficient time to cause recrystallization. Distributed within the wire are a plurality of minute segregations, and substantially all of these segregations are aligned into segregation groupings. These aligned segregations, which comprise thorium oxide and are of varying size, are aligned in single file and are quite similar to what may be termed stringers. The ASM metals handbook, 1948 edition, defines stringers as "A microstructural configuration of alloy constituents or foreign material lined up in the direction of working." This definition closely fits the aligned segregation groupings as shown in FIGS. 4, 5, 6 and 7 except that the term "stringer" normally infers a continuous and elongated inclusion aligned in the direction of working. For this reason, it is considered more correct to define the aligned and dot-like segregations as a plurality of discontinuous stringer-like segregation groupings which are formed by substantially all the minute segregations included in the wire. The minute segregations are normally circular in configuration, although some may be slightly elongated in the direction of working. As seen in the photomicrographs of FIGS. 5 and 6, the highly-magnified tungsten crystals are of an interlocking nature and are elongated, with the elongated crystal dimensions generally following the disposition of the discontinuous stringer-like segregation groupings. Since the primary difference between the interlocking crystal structure of the instant filament and the interlocking crystal structures of the prior art are the discontinuous stringer-like segregation groupings, it is apparent that these segregation groupings maintain the crystals in their interlocking relationship to provide excellent shock-resistant, vibration-resistant and non-sag characteristics for the filament.

In FIG. 7 is shown an etched section of the same portion of the wire as shown in FIG. 6, except that the magnification is 2000× and this better illustrates the disposition of the minute segregations within the wire. As seen in this high-magnification photomicrograph, only a few of the segregations are randomly distributed within the wire, that is, not aligned into the segregation groupings and substantially all of the minute segregations included within the wire are aligned into the discontinuous stringer-like segregation groupings.

In FIG. 8 is shown a photomicrograph (250×) of an etched section of thoria-doped wire, after recrystallization, which wire is representative of an ingot sintered at 87% of its fusion current for a period of twenty-five minutes. This photomicrograph was taken at too low a magnification to show the general distribution of the minute segregations which are included within the wire. It does illustrate, however, the random crystal structure, which approaches what is known in the art as an equiax structure, which is obtained after the wire is recrystallized. This photomicrograph is to be contrasted with the photomicrograph of FIG. 5.

In FIG. 9 is shown a photomicrograph (1000×) of an etched section of thoria-doped wire, similar to that shown in FIG. 8, but with a greater magnification. As shown, the minute segregations are distributed throughout the wire in a relatively-random fashion. While some of the segrations have remained in the aligned groupings, a considerable portion have migrated into a generally-random distribution throughout the wire.

The generally-random distribution of a considerable portion of the segregations included in such wire is better illustrated in the photomicrograph shown in FIG. 10, which is of the same section of the wire as shown in FIG. 9, but with a still-higher magnification (2000×). As clearly shown in this photomicrograph, a considerable portion of the minute segregations are scattered in random fashion throughout the wire.

It is very difficult to determine actual particle sizes of the minute segregations within the wire when using an etching and photomicrograph technique, since some of the tungsten around the etched particles is also dissolved. This gives a false impression of the actual size of the segregations. However, it is clear from an observation of the photomicrographs shown in FIGS. 6, 7, 9 and 10 that where the thoria-doped ingot is sintered at such current and for such time so as to cause the plot of sintering current vs. time to fall on or above the curve A–B in FIG. 2, some of the segregations included within the resulting wire are somewhat coagulated, as compared to the segregations included within wire processed according to the instant teachings. This is in addition to being considerably random in distribution within the wire. Such filament wire as shown in FIGS. 8, 9 and 10, when incorporated into an incandescent lamp, will sag very rapidly, apparently because of slippage at the crystal boundaries. The photomicrographs shown in FIGS. 4 through 10 were taken of wire which had been drawn to a diameter of 0.043 inch. The appearance of the wire at this diameter is representative of the appearance of such wire drawn to a smaller diameter, except that the longitudinal distance between the individual segregations increases as the wire is drawn to a smaller size.

As noted hereinbefore, the percent by weight of thorium oxide may vary from ¼% to 4% by weight of the tungsten. At less than ¼% by weight thorium oxide, the beneficial effects which are realized through the stringer-like segregation groupings are minimized and at more than 4% by weight thorium oxide, difficulties are encountered in swaging the ingot. It is preferred to use from ¾% to 1½% by weight of the tungsten of thorium oxide as a doping additive. Within this preferred range, few difficulties are encountered in swaging the ingot and there is sufficient doping additive present to provide maximum benefit with respect to shock-resistant, vibration-resistant and non-sag characteristics for the filment wire.

In the foregoing specific example, the sintering and annealing atmosphere is dry hydrogen. The dry hydrogen as used has a dewpoint of about minus 60° F. It should be understood that hydrogen containing appre-

ciably more moisture can be tolerated. Also, hydrogen containing substantially no moisture can be used and the foregoing moisture content of the hydrogen has been given only by way of example. It is also possible to use other non-oxidizing atmospheres in sintering and annealing, such as rare gas atmospheres, or even vacuum, but it is economically desirable to use hydrogen.

Vibration and shock resistance for incandescent filaments is best measured on a performance basis. In one test which simulates the shocks to which toy train lamps are subjected, the lamps are mounted on a metallic plate. The plate is then struck a series of impacts under carefully-controlled conditions. Lamps which incorporated the instant filaments were mounted in this shock tester and were subjected to 1000 shocks. At the end of this test, 76% of the lamps incorporating the instant improved filament would still operate. Similar lamps which were provided with the prior-art potassium, alumina and silica-doped wire were mounted in the shock tester and after 1000 impacts, only 8% of these prior-art lamps would still operate. While the test was extremely severe, it nevertheless simulates the shocks to which such lamps are subjected when they are used and the performance test illustrates the almost phenomenal strength which the instant non-sag wire possesses. Other applications which require a very high-strength wire are automobile radio and panel lighting and automobile trunk lights where the lamps are subjected to the shocks of automobile vibrations and the trunk being slammed shut. In all tests simulating the shocks and vibrations which lamps receive in such applications, the instant wire displays an outstanding superiority over the best-available shock- and vibration-resistant, non-sag wire of the prior art. It should be noted that the instant wire operates with slightly less efficiency than the best prior-art doped wire. It is not possible, however, even to approach the performance of the instant improved wire by operating the best prior-art doped wire at a lower temperature, which simulates lower operational efficiency.

As noted hereinbefore, thoria doping of tungsten has been reported many times, with the patent and other art extending back to the early 1900's. The best of these thoria-doping techniques, however, produced wire which was subject to considerable sag and the general performance of such thoria-doped wire is summarized in Patent No. 2,114,426 to Laise. It was primarily for these reasons that the thoria-doped wire was replaced by the presently-used potassium, alumina and silica-doped wire. Thoria-doped tungsten has also been used in fabricating welding electrodes where the electron-emissivity of the thoria facilitates striking and maintaining the welding arc. In the prior-art processing for thoria-doped tungsten, the best-accepted procedure has been to sinter the ingots at a maximum current of about 87% to 92% of the ingot fusion current and to maintain this maximum sintering current for about twenty-five minutes. As shown in FIG. 2, this will not produce a material which can be swaged and drawn to form shock-resistant, vibration-resistant and non-sag filament wire for incandescent lamps. In the foregoing shock and vibration tests, the best thoria-doped tungsten filaments of the prior art would be generally suitable from the standpoint of shock and vibration resistance. Lamps incorporating such filaments, however, would fail quickly from filament sag since the usual filament design will not tolerate any appreciable sag.

The processing of the instant wire involves a temperature-time phenomenon, wherein the temperature parameter, during sintering, has been represented as ingot sintering current, expressed as a percentage of ingot fusion current. At excessively high sintering temperatures which are maintained for an appreciable sintering period, swaging and drawing such a sintered ingot will not produce the stringer-like groupings in the resulting filament wire, which stringer-like groupings are required to direct the crystal growth into an interlocking structure and maintain same during lamp operation. Thus to produce the instant wire, the sintering current-time relationships must be kept relatively low, as compared to the practices of the prior art. It should be noted that X-ray diffraction studies of the instant wire disclose only the presence of thoria and tungsten. The presence of some limited amounts of thoium-tungsten complexes should not be excluded, however, even though these are not indicated in the X-ray diffraction studies. In addition, some impurities in the doping material may be tolerated and these have not been observed to affect deleteriously the quality of the wire.

It has been found that the instant wire will best perform in the exceptional manner indicated hereinbefore when the lamps in which it is used are of a type which operate with a relatively low efficiency, such as miniature types as used in panel lighting, toy trains, etc. The filament operating temperatures for such lamps are in the order of about 2050° C. to about 2430° C., as contrasted with a standard gas-filled 100-watt lamp which operates at a filament temperature of about 2600° C. In the operation of lamps incorporating the instant improved wire, the temperature-time relationship which governs the formation of the discontinuous, stringer-like segregation groupings is also present and the higher the operating temperature of the lamps, the faster the segregations depart from the stringer-like formations to a random disposition. When an appreciable portion of the stringer-like formations of segregation groupings have migrated to form random segregations, the crystals within the wire grow further, the interlocking structures disappear, and at this point the filament sags and fails through shorting out turns of the filament coil.

The foregoing observations are substantiated by further control studies. As the miniature-type, low-efficiency lamps which incorporate the instant wire are operated, their performance is excellent under conditions of vibration and shock. Between 1000 and 1500 hours, an appreciable portion of the stringer-like groupings disappear and form randomly distributed particles and when this occurs, the wire sags and the lamp fails. This temperature-time dependence for the migration of the segregations from the stringer-like groupings is additionally substantiated by incorporating the instant wire into so-called high-efficiency lamps where the filament is operated at a much higher temperature. Here the performance of the instant wire, from the standpoint of life, is not as good and the lamp filament sags and fails at an earlier time. At failure of both the low-efficiency and high-efficiency lamps, photomicrographs of the etched filaments which failed show a migration of a considerable portion of the stringer-like segregation groupings into random particles or segregations.

While the instant wire when used in so-called high-efficiency lamps will result in relatively short lamp life, it should be understood that shorter life for high efficiency lamps is not objectionable in all cases, particularly where shock and vibration resistance are of prime importance. For some applications, a shorter lamp life can be tolerated for the sake of the other attributes of the instant wire. Again it is pointed out that the instant non-sag filament wire is almost phenomenal in its strength under vibration and shock and far surpasses any filament wire heretofore reported.

In the foregoing specific example, thorium nitrate was added to the ammonium paratungstate before the paratungstate was converted to tungstic oxide. Thorium compounds which convert to the oxide on heating can be substituted for the thorium nitrate, specific examples being thorium hydroxide or thorium oxalate, using dry-mix techniques where necessary. Also, thorium oxide can be added as such to the ammonium paratungstate. In addition, any of the aforementioned thorium-containing compounds, for example, can be added directly to the tungstic oxide or even to the tungsten metal powder. In a case

of thorium compounds other than thorium oxide, the addition of such compounds to the tungsten metal powder will normally necessitate an additional conversion step to convert the material to thorium oxide. In addition, tungsten metal powder and ammonium paratungstate or other tungsten-containing compound which is reducible to tungsten metal powder can be admixed in forming the initial admixture, prior to forming the green ingot. As an example, equal parts by weight of tungsten metal powder and ammonium paratungstate can be used in forming the initial admixture. Also, the thorium-containing compounds which are convertible to thorium oxide can be admixed as doping material, such as an admixture of equal proportions of thorium nitrate and thorium hydroxide. It should be understood that in all cases the weight ratio of thorium, expressed as the oxide, to tungsten should be maintained within the aforementioned thorium oxide to tungsten limitations. It is thus apparent that the essential steps of the process involve forming an admixture of thorium oxide and tungsten metal powder within the aforementioned constituent weight percentages, forming the green ingot, sintering the green ingot at the effective sintering currents in accordance with the schedules established by the curves A–B or C–D in FIG. 2, and thereafter reducing the sintered ingot into wire of the desired size. It is preferred, however, to add the thorium nitrate to the ammonium paratungstate, as given in the foregoing specific example.

A consideration of the curves A–B and C–D in FIG. 2 will show that only the maximum sintering currents have an appreciable effect on the current-time relationships which are present during sintering and which affect the later performance of the filament wire. It is possible to use a "step-ladder" sintering procedure at the effective sintering currents, wherein the effective sintering currents may be varied and held for relatively short periods of time. If a "step-ladder" type of sintering schedule at the higher effective ingot sintering currents is to be used, the summation of percentages of ingot sintering times for the ingot sintering currents used should be less than 100%, where the 100% abscissa value corresponding to any ingot sintering current, expressed as a percent of ingot fusion current, is established by the corresponding abscissa values of the curves A–B or C–D in FIG. 2, depending on whether a permissible or preferred sintering schedule is desired. As an example, if an ingot is sintered at 71% of fusion amperes for a period of twenty minutes, it will have been sintered for approximately 11% of the maximum permissible sintering time at this current. Thereafter, if the ingot sintering current is increased to 75% of fusion amperes and the ingot is sintered for twenty minutes at this sintering current, it will have been sintered for approximately 25% of the maximum permissible sintering time at this sintering current. Thereafter, if the ingot sintering current is increased to 78% of fusion amperes and it is sintered at this current for approximately ten minutes, it will have been sintered for approximately 22% of the maximum permissible sintering time at this sintering current. Finally the ingot may be sintered at a current of 80% of fusion amperes for six minutes, which represents approximately 18% of the maximum permissible sintering time at this sintering current. Adding the foregoing percentages, the ingot will have been sintered for a total of 76% of its maximum permissible sintering, if wire in accordance with the instant teachings is to result. As an example of a "step-ladder" sintering process for the preferred sintering schedule, 70% of fusion amperes for twenty minutes, then 75% of fusion amperes for ten minutes, then 78% of fusion amperes for six minutes and finally 80% of fusion amperes for five minutes will result in the ingot having been sintered for approximately 81% of its maximum preferred sintering.

The fusion current for the doped ingot will vary somewhat with the doping constituents. As an example, where the ingot is doped with the prior-art potassium, alumina and silica-doping constituents, the ingot fusion temperature is somewhat lower than for a corresponding thoria-doped ingot. This is probably because these prior-art doping constituents normally result in increasing the electrical resistance of the ingot. With a higher electrical resistance, less sintering current is required to produce the same temperature, so that the current required for fusion of the ingot is slightly lower. In thoria-doped wire, the concentration of residual doping material after sintering is approximately the same as the concentration of the doping material before sintering. This is contrary to the usual prior-art wire, which as an example may contain residual doping material, after sintering, in concentrations of 1000 parts per million alumina, 1000 parts per million silica and 100 to 400 parts per million potassium. Experiments have been conducted wherein equal proportions of thoria-doped tungsten metal powder and the prior-art potassium, alumina and silica-doped tungsten metal powder were admixed and sintered in accordance with a schedule which would produce the instant non-sag vibration- and shock-resistant wire. Since most of the alumina, silica and potasium are volatilized during the sintering, the thoria-doping predominates and satisfactory shock- and vibration-resistant, non-sag wire is produced. The fusion current for such an admixed green ingot is slightly lower, but the current-time relationships as shown in the curves A–B or C–D in FIG. 2 must still be followed. Thus the instant wire may be produced where the green ingot contains only an appreciable proportion of the thoria, as doping material, provided the percentages of the thoria with respect to the total tungsten metal are maintained within the aforementioned ranges. In addition, the presence of other refractory oxides added as doping constituents may be tolerated in the instant wire. As an example, 10% by weight of the thoria of ceria has not been found to effect deleteriously the performance of the instant wire.

The preferred ingot sintering technique, as detailed hereinbefore, is an electrical sintering technique, wherein a high current is passed through the green ingot to effect the sintering. This may be defined as electrical-resistance sintering. Ingot sintering may also be accomplished by an induction-heating technique using an ingot as specified hereinbefore, for example, and effecting the sintering in a non-oxidizing atmosphere, preferably hydrogen, in a manner as detailed heretofore. Where induction-heating sintering of the ingot is used, the effective ingot sintering temperatures should be the same as where electrical-resistance ingot sintering is used, since the formation of the instant wire is dependent upon a temperature-time sintering schedule, as explained in detail. In order to correlate induction-heating sintering schedules with electrical-resistance sintering schedules, the electrical-resistance sintering bottle may be provided with a protected sighting window through which optical pyrometer temperature readings of the ingot may be correlated with ingot sintering current, expressed as a percent of ingot fusion current. Induction-heating apparatus suitable for sintering a green ingot is commercially available. In correlating the induction-heating schedules, a protected sighting window may also be provided through the induction-heating furnace. With the same-size ingot and the same dry-hydrogen atmosphere during sintering, the same effective ingot sintering temperatures must be maintained for the same times as where an electrical-resistance sintering technique is used, if the instant wire is to be produced. Accordingly, proper induction-heating sintering schedules may be correlated by the optical pyrometer ingot sintering temperatures previously taken. Thus when using an induction-heating technique for sintering the green ingot to produce the instant wire, the ingot should be sintered at such temperature and for such time that the sintered ingot can be

mechanically reduced in size wihout fracturing. In addition, the effective ingot sintering temperatures should be those which are obtained with an electrical-resistance sintering technique. These effective sintering temperatures may be expressed as equivalent ingot sintering currents in terms of percent of ingot fusion current which, when plotted vs. time in minutes that the sintering temperature (expressed as current) is maintained, must fall below the curve A–B or C–D in FIG. 2, depending on whether a permissible or preferred sintering schedule is to be used.

It should be understood that while specific sintering schedules have been outlined for an ingot of specific dimensions, varying the ingot dimensions will alter the fusion current for the ingot and thus alter the specific sintering currents as given hereinbefore. However, the ingot sintering currents, when expressed as a percent of ingot fusion current, are for practical purposes independent of the ingot dimensions. Thus the permissible and preferred ingot sintering schedules established by the curves A–B and C–D in FIG. 2 are for practical purposes independent of ingot dimensions.

In the foregoing description, specific ingot dimensions and characteristics as well as specific sintering schedules were outlined in detail. It should be clear that the specific ingot dimensions, sintering techniques and schedules can be modified, provided the ingot sintering temperature (as expressed by current) vs. time relationships as established by the curves A–B and C–D in FIG. 2 are followed. Thus no matter what the ingot sintering technique or schedule, the green ingot should be sintered at such temperature and for such time that the resulting sintered ingot can be mechanically reduced in size without fracturing. In addition, the ingot sintering temperatures and ingot sintering times should be equal to those ingot sintering temperatures and ingot sintering times which are obtained when electrical-resistance sintering an ingot as detailed hereinbefore, with the plot of ingot sintering current expressed as a percent of ingot fusion current falling below the curve A–B or C–D, depending on whether a permissible or preferred sintering schedule is to be followed. Ingot sintering temperatures may be correlated with an optical pyrometer technique, as described hereinbefore. Thereafter the sintered ingot may be formed into wire by swaging and drawing as described in detail hereinbefore.

It will be recognized that the objects of the invention have been achieved by providing shock-resistant, vibration-resistant and non-sag filament wire and filaments suitable for use in incandescent lamps, which filaments comprise a plurality of interlocking crystals which are maintained as such during operation of the lamp. In addition, there have been provided a process for forming such filament wire, including permissible and preferred process steps and conditions for forming such wire.

While in accordance with the patent statutes, one best embodiment of the invention has been illustrated and described in detail, it is to be particularly understood that the invention is not limited thereto or thereby.

I claim:

1. A shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps, said wire comprising from 96% to 99¾% by weight tungsten and from 4% to ¼% by weight thorium oxide, a plurality of minute segregations comprising said thorium oxide distributed within said wire, and a plurality of discontinuous stringer-like segregation groups formed by substantially all of said minute segregations and distributed throughout said wire.

2. A shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps, said wire comprising from 98½% to 99¼% by weight tungsten and from 1½% to ¾% by weight thorium oxide, a plurality of minute segregations comprising said thorium oxide distributed within said wire, and a plurality of discontinuous stringer-like segregation groupings formed by substantially all of said minute segregations and distributed throughout said wire.

3. A shock-resistant, vibration-resistant and non-sag filament for incandescent lamps, comprising a wire coiled in a generally-helical configuration, said wire comprising from 96% to 99¾% by weight tungsten and from 4% to ¼% by weight thorium oxide, a plurality of minute segregations comprising said thorium oxide distributed within said wire, and substantially all of said segregations aligned in a plurality of discontinuous stringer-like groupings disposed throughout said wire.

4. A shock-resistant, vibration-resistant and non-sag filament for incandescent lamps, comprising a wire coiled in a generally-helical configuration, said wire comprising from 98½% to 99¼% by weight tungten and from 1½% to ¾% by weight thorium oxide, a plurality of minute segregations comprising said thorium oxide distributed within said wire, and substantially all of said segregations aligned in a plurality of discontinuous stringer-like groupings disposed throughout said wire.

5. A shock-resistant, vibration-resistant and non-sag recrystallized filament for incandescent lamps, said filament comprising a wire coiled in a generally-helical configuration, said wire comprising a plurality of interlocking crystals and containing from 96% to 99¾% by weight tungsten and from 4% to ¼% by weight thorium oxide, a plurality of minute segregations comprising said thorium oxide distributed within said wire, a plurality of discontinuous stringer-like segregation groupings formed by substantially all of said minute segregations, and the interlocking crystals of said wire being elongated with the elongated crystal dimensions generally following the disposition of said segregation groupings.

6. A shock-resistant, vibration-resistant and non-sag recrystallized filament for incandescent lamps, said filament comprising a wire coiled in a generally-helical configuration, said wire comprising a plurality of interlocking crystals and containing from 98½% to 99¼% by weight tungsten and from 1½% to ¾% by weight thorium oxide, a plurality of minute segregations comprising said thorium oxide distributed within said wire, a plurality of discontinuous stringer-like segregation groupings formed by substantially all of said minute segregations, and the interlocking crystals of said wire being elongated with the elongated crystal dimensions generally following the disposition of said segregation groupings.

7. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps, comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¼% to 4% by weight of the admixed tungsten, forming said admixture into a self-sustaining green ingot, electrically sintering said green ingot under non-oxidizing conditions at such sintering current and for such time that the resulting sintered ingot can be mechanically reduced in size without fracturing and so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time falls below the curve A–B in FIG. 2, and thereafter reducing said sintered ingot into wire of the desired size.

8. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps, comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¾% to 1½% by weight of the admixed tungsten, forming said admixture into a self-sustaining green ingot, electrically sintering said green ingot under non-oxidizing conditions at such sintering current and for such time that the resulting sintered ingot can be mechanically reduced in size without fracturing and so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time falls below the curve

C–D in FIG. 2, and thereafter reducing said sintered ingot into wire of the desired size.

9. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps, comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¼% to 4% by weight of the admixed tungsten, forming said admixture into a self-sustaining green ingot, electrically sintering said green ingot in a hydrogen atmosphere at such sintering current and for such time that the density of the sintered ingot is at least about 16.4 and so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time falls below the curve A–B in FIG. 2, and thereafter reducing said sintered ingot into wire of the desired size.

10. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps, comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¾% to 1½% by weight of the admixed tungsten, forming said admixture into a self-sustaining green ingot, electrically sintering said green ingot in a dry-hydrogen atmosphere at such sintering current and for such time that the density of the sintered ingot is at least about 17.1 and so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time falls below the curve C–D in FIG. 2, and thereafter mechanically reducing said sintered ingot into wire of the desired size.

11. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps: comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¼% to 4% by weight of the admixed tungsten; forming said admixture into a self-sustaining green ingot; electrically sintering said green ingot under non-oxidizing conditions at such ingot sintering currents and for such time that the resulting sintered ingot can be mechanically reduced in size without fracturing, and so that the summation of percentages of ingot sintering times for the effective ingot sintering currents are less than 100%, where the 100% abscissa value corresponding to any ingot sintering current, expressed as a percent of ingot fusion current, is established by the corresponding abscissa value of the curve A–B in FIG. 2; and thereafter mechanically reducing said sintered ingot into filament wire of the desired size.

12. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps: comprising forming an admixture of at least one of the group consisting of finely-divided tungsten metal powder and tungsten-containing compound which is reducible to tungsten metal powder, and doping material comprising at least one of the group consisting of finely-divided thorium oxide and finely-divided thorium-containing compound which is convertible to thorium oxide; the percent by weight of admixed thorium-compound doping material expressed as thorium oxide being from ¾% to 1½% by weight of the tungsten expressed as metal; converting thorium-containing compound into thorium oxide; reducing tungsten compound to tungsten metal powder; forming said admixed tungsten metal powder and doping material into a self-sustaining green ingot; electrically sintering said green ingot under non-oxidizing conditions at such ingot sintering currents and for such time that the resulting sintered ingot can be mechanically reduced in size without fracturing, and so that the summation of percentages of ingot sintering times for the effective ingot sintering currents are less than 100%, where the 100% abscissa value corresponding to any ingot sintering current, expressed as a percent of ingot fusion current, is estabilshed by the corresponding abscissa value of the curve C–D in FIG. 2; and thereafter mechanically reducing said sintered ingot into filament wire of the desired size.

13. The process of forming shock-resistant, vibration-resistant and non-sag filament wire for use in incandescent lamps, comprising forming an admixture of finely-divided ammonium paratungstate and finely-divided thorium nitrate, the percent by weight of thorium nitrate expressed as thorium oxide being from ¾% to 1½% by weight of the admixed tungsten compound expressed as tungsten metal, converting said ammonium paratungstate to tungstic oxide and converting said thorium nitrate to thorium oxide, reducing said tungstic oxide to tungsten metal powder, forming said admixed tungsten metal powder and thorium oxide into a self-sustaining green ingot, electrically sintering said green ingot in a dry-hydrogen atmosphere at such sintering current and for such time that the density of the sintered ingot is at least about 16.4 and so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time falls below the curve C–D in FIG. 2, and thereafter mechanically reducing said sintered ingot into wire of the desired size.

14. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps, comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¼% to 4% by weight of the admixed tungsten, forming said admixture into a self-sustaining green ingot, electrically sintering said green ingot under non-oxidizing conditions at such sintering current and for such time that the resulting sintered ingot can be mechanically reduced in size without fracturing and so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time in minutes falls below the curve represented by the formula:

$$\text{sintering current} = 70 + (14.8)(e^{-t/67}) + (11.2)(e^{-t/11.5})$$

where "t" is expressed in minutes and is at least 2, and thereafter reducing said sintered ingot into wire of the desired size.

15. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps, comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¾% to 1½% by weight of the admixed tungsten, forming said admixture into a self-sustaining green ingot, electrically sintering said green ingot in a dry-hydrogen atmosphere at such sintering current and for such time that the resulting sintered ingot may be mechanically reduced in size without fracturing and so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time in minutes falls below the curve represented by the formula:

$$\text{sintering current} = 69.5 + (8.3)(e^{-t/80}) + (10.4)(e^{-t/18.5})$$

where "t" is expressed in minutes and is at least 5, and thereafter reducing said sintered ingot into wire of the desired size.

16. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps: comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¼% to 4% by weight of the tungsten; forming said admixture into a self-sustaining green ingot; sintering said green ingot under non-oxidizing conditions at such temperature and for such time that said sintered ingot can be mechanically reduced in size without fracturing, and so that the ingot sintering temperatures are those as obtained with an electrical-resistance sintering technique with the plot of ingot sintering temperature, expressed as equivalent ingot sintering current in terms

of percent of ingot fusion current, vs. time falling below the curve A–B in FIG. 2; and thereafter reducing said sintered ingot into wire of the desired size.

17. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps: comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¾% to 1½% by weight of the tungsten; forming said admixture into a self-sustaining green ingot; sintering said green ingot in a dry-hydrogen atmosphere at such temperature and for such time that said sintered ingot can be mechanically reduced in size without fracturing, and so that the ingot sintering temperatures are those as obtained with an electrical-resistance sintering technique with the plot of ingot sintering temperature, expressed as equivalent ingot sintering current in terms of percent of ingot fusion current, vs. time falling below the curve C–D in FIG. 2; and thereafter reducing said sintered ingot into wire of the desired size.

18. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps: comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¼% to 4% by weight of the tungsten; forming said admixture into a self-sustaining green ingot; sintering said green ingot at such temperatures and for such times that the resulting sintered ingot can be mechanically reduced in size without fracturing and so that the ingot sintering temperatures and ingot sintering times are equal to those ingot sintering temperatures and ingot sintering times obtained when electrical-resistance sintering a green ingot so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time falls below the curve A–B in FIG. 2, wherein the electrical-resistance-sintered ingot has green ingot dimensions of 0.725 inch by 0.655 inch by 24 inches and an ingot fusion current of 6700 amperes; and thereafter reducing said sintered ingot into wire of the desired size.

19. The process of forming shock-resistant, vibration-resistant and non-sag filament wire suitable for use in incandescent lamps: comprising forming an admixture of tungsten metal powder and doping material comprising thorium oxide, the percent by weight of thorium oxide being from ¾% to 1½% by weight of the tungsten; forming said admixture into a self-sustaining green ingot; sintering said green ingot at such temperature and for such time that the resulting sintered ingot can be mechanically reduced in size without fracturing and so that the ingot sintering temperatures and ingot sintering times are equal to those ingot sintering temperatures and ingot sintering times obtained when electrical-resistance sintering a green ingot so that the plot of ingot sintering current expressed as a percent of ingot fusion current vs. time falls below the curve C–D in FIG. 2, wherein the electrical-resistance-sintered ingot has green ingot dimensions of 0.725 inch by 0.655 inch by 24 inches and an ingot fusion current of 6700 amperes; and thereafter reducing said sintered ingot into wire of the desired size.

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L. DEWAYNE RUTLEDGE, *Primary Examiner.*

ROGER L. CAMPBELL, WILLIAM G. WILES, *Examiners.*

O. R. VERTIZ, R. L. GRUDZIECKI, *Assistant Examiners.*