Aug. 11, 1959 R. L. HOFF 2,899,301

TUNGSTEN-TANTALUM-NICKEL CATHODES

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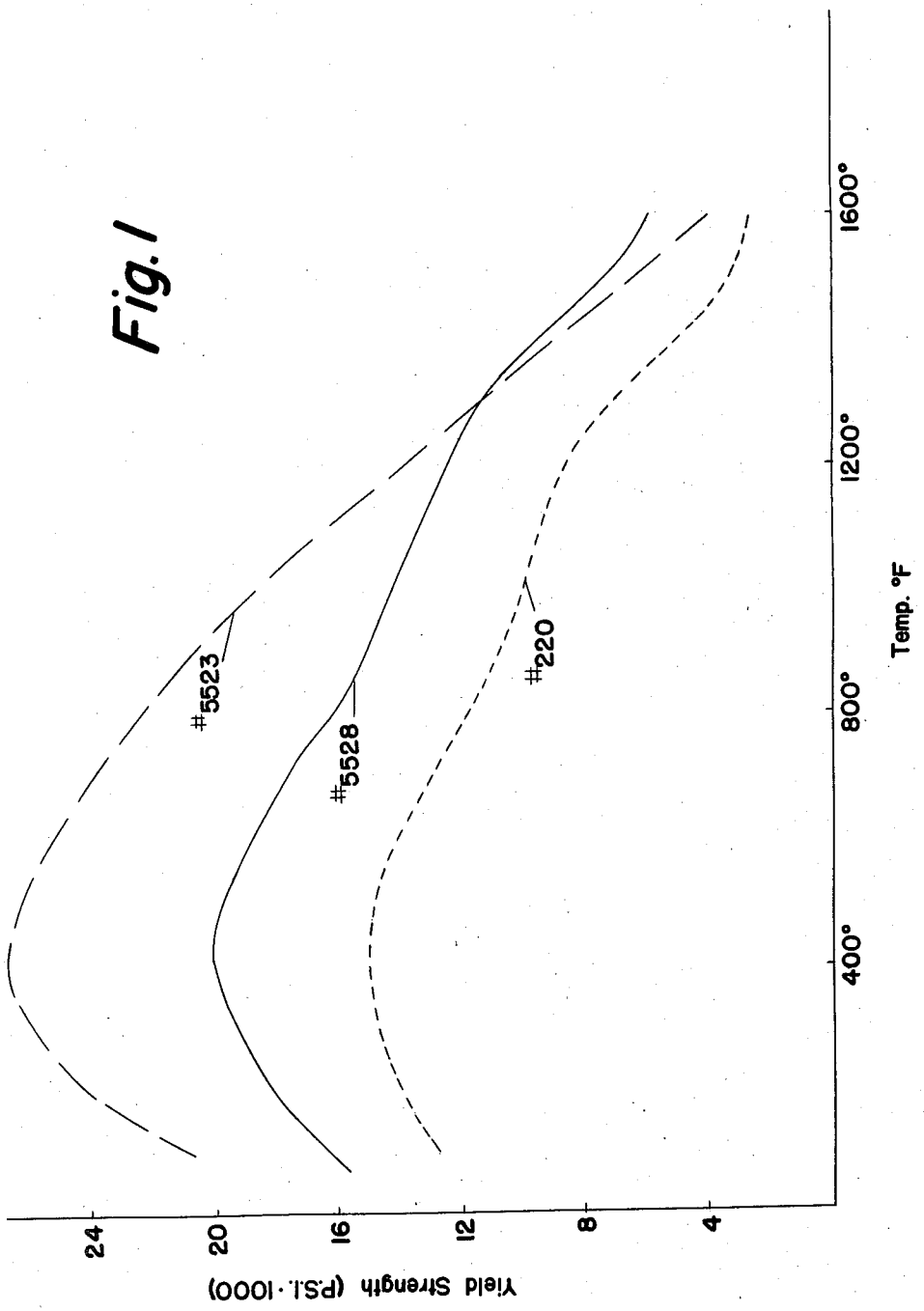
Fig. 1



TUNGSTEN-TANTALUM-NICKEL CATHODES

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Fig. 2A

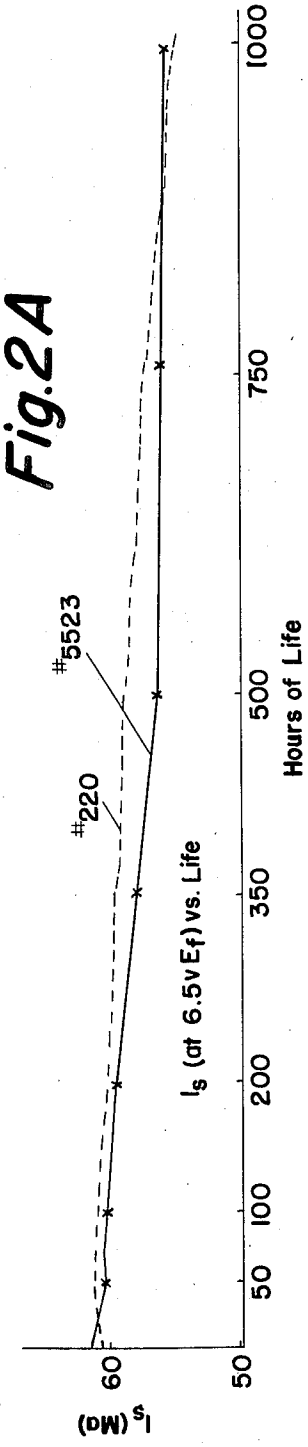
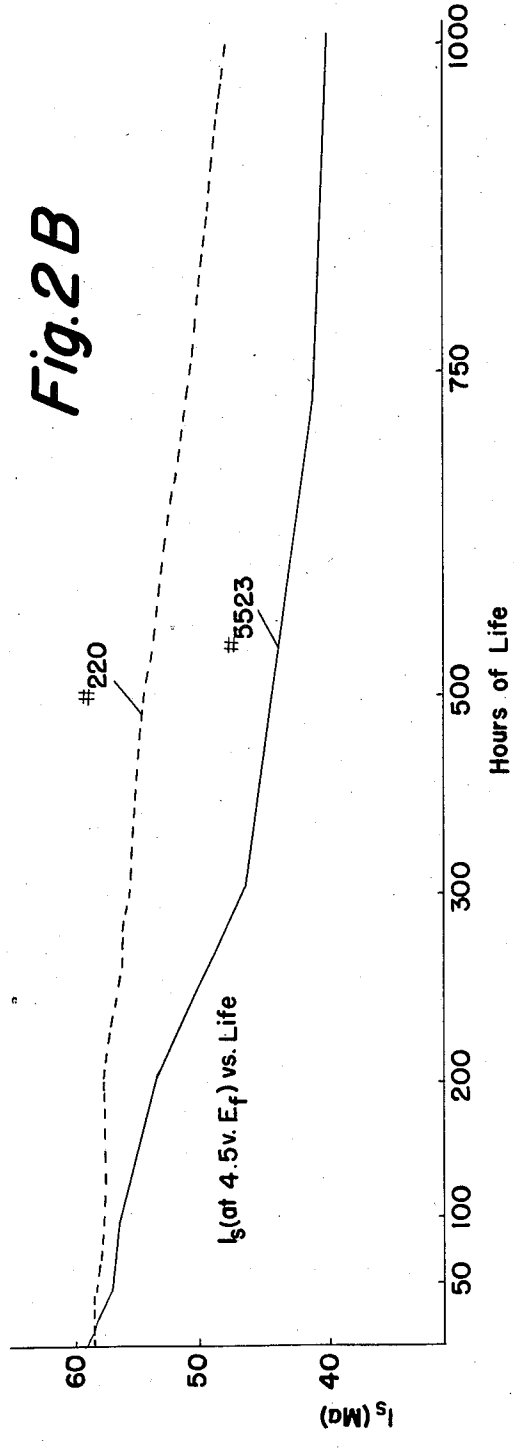


Fig. 2B



TUNGSTEN-TANTALUM-NICKEL CATHODES

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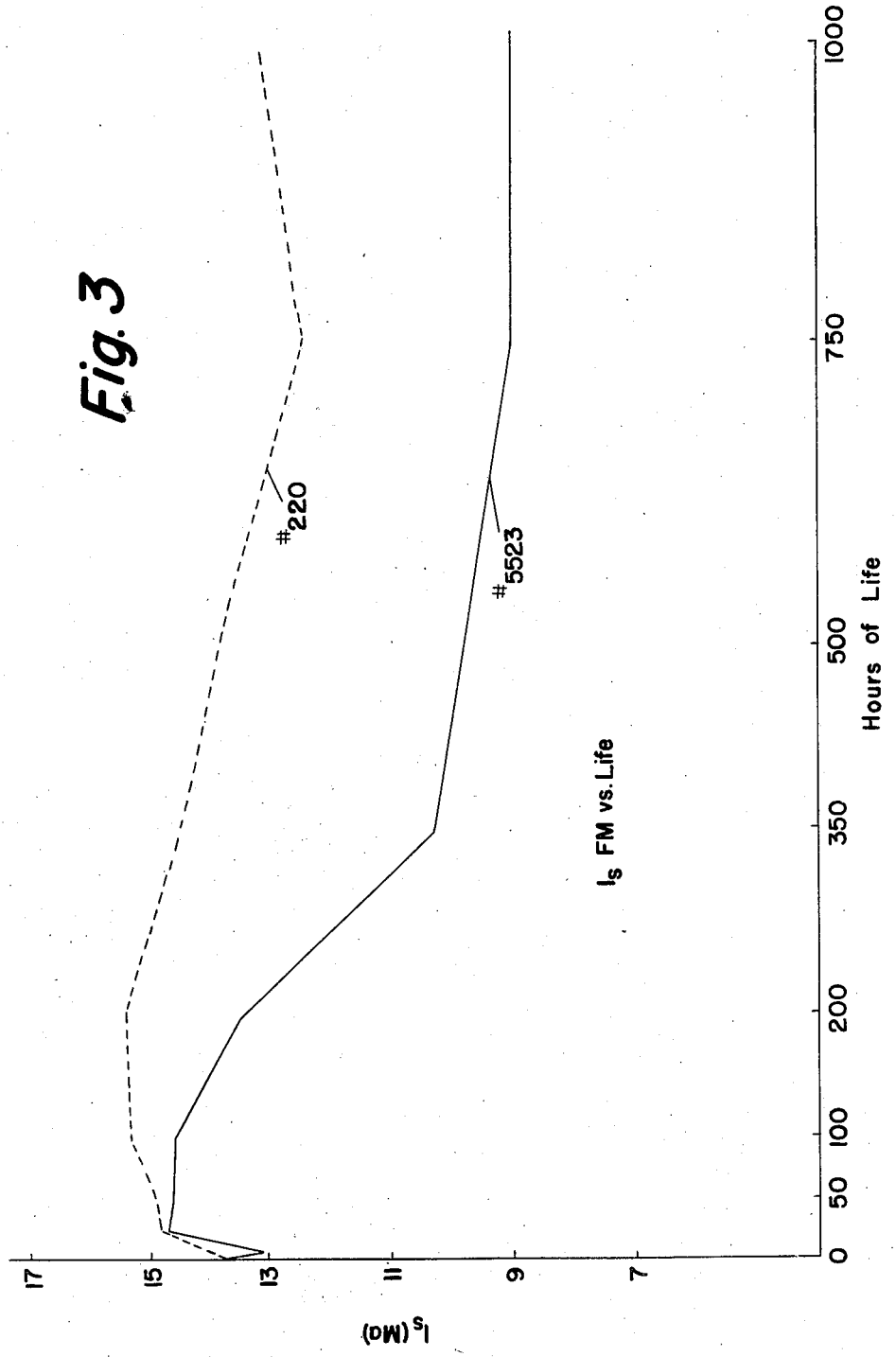
Fig. 3



United States Patent Office

2,899,301

Patented Aug. 11, 1959

2,899,301

TUNGSTEN-TANTALUM-NICKEL CATHODES

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Application August 26, 1957, Serial No. 680,081

3 Claims. (Cl. 75—170)

This invention relates to cathodes of the indirectly-heated type for electron tubes.

In general, the object of the invention is to provide indirectly-heated cathodes which have substantially enhanced resistance to deformation when subjected to shock or vibration at their elevated operating temperatures and which have good emission and sublimation characteristics substantia'ly equivalent to or better than those of prior nickel alloy cathodes.

In accordance with the present invention, such dual objective is attained by making the cathode sleeves, cups or the like from a nickel alloy which includes, within narrow percentage ranges herein specified, the additives tungsten and tantalum. Considering all of the many factors involved, the preferred composition contains about 4% tungsten, about 0.1% tantalum and the remainder essentially nickel.

In the following description, reference is made to the accompanying drawings in which:

Fig. 1 is a group of curves exemplary of the yield strength, throughout a temperature range including cathode-operating temperatures, of specific tungsten-tantalum-nickel alloys and of a reference nickel alloy; and

Figs. 2A, 2B and 3 comprise groups of curves referred to in discussion of emission characteristics of indirectly-heated cathodes made from the reference nickel alloy and from nickel alloys including the additives tungsten and tantalum.

In general, indirectly-heated cathodes consist of a nickel alloy base element, such as a sleeve or cup, having thereon a thin coating of alkaline earth metals such as barium, strontium or the like. The fabrication of the alloy stock into cathode base elements involves hot and cold working steps, such as forging, rolling, drawing, stamping and the like. After assembly of the coated cathode, including its heater and other electrodes within an envelope to form an electronic tube, the cathode is activated by temporarily heating it substantially above its normal operating temperature. During activation, there are reactions between the base element alloy materials and the coating materials which convert the coating to a combination of complex oxides which emit electrons when heated to cathode-operating temperatures in the neighborhood of 1600° F. In the more usual services, the effective life of the tube is terminated when its cathode emission is definitely subnormal at normal heater current. However, for many uses, including field applications where the available source voltage is low or fluctuating, tubes are considered unfit when their cathode emission is substantially affected by low or varying heater current.

The operating life of a tube is also affected by cathode characteristics other than electron emission. For example, the normal life of high-voltage rectifier tubes has often abruptly terminated because of eruptive flaking or peeling of the cathode coating from the cathode sleeve. Also, the operation of amplifier, oscillator and mixer tubes has been adversely affected by formation and continued growth of a high-impedance interface between the

cathode sleeve and its coating. The resistive component of such interface impedance is damaging, particularly in pulse-type operation, even at ordinary frequencies; the capacitive component of such interface impedance is particularly damaging at high frequencies, even when the tube is not operated under pulsed or cut-off conditions. The life of a tube may also be terminated by the formation, from material sublimed from its cathode, of a leakage path between electrodes of the tube. The operating life of a tube is also determined by the mechanical properties of its cathode element; for example, cathode sleeves made of the usual nickel alloys often bowed when subjected to high temperatures during their activation period, so causing internal short-circuits or significant changes in interelectrode spacing. Also in services where the tubes are subjected to severe mechanical shock, as in airborne missile equipment, buckling or deformation of their cathode sleeves rendered the tubes inoperative before performance of their intended function.

I have determined that the addition of tungsten and tantalum, within the narrow percentage ranges later herein specified, to nickel cathode stock provides cathode alloys which are amenable to both hot and cold-working and which as fabricated into indirectly-heated cathodes afford rapid activation, sustained high emission levels, virtual freedom from sublimation, negligible interface impedance, and a hot strength substantially exceeding that of nickel cathode alloys.

Considering first the enhancement of hot strength at cathode-operating temperatures of about 1600° F., the addition of tungsten in the range of 1 to 5% and tantalum in the range of 0.05% to 2% to nickel cathode stock substantially increases the hot strength. In this range, the addition of a small amount of tantalum is more effective in increasing hot strength than the addition of a larger amount of tungsten. For example, a binary tungsten nickel alloy containing 2% tungsten has a yield strength at about 1600° F. of 3800 p.s.i. (pounds per square inch) at a test loading rate of 0.004 inch per minute. Increasing the tungsten percentage to 4% increases the hot strength at about 1600° F. to 4100 p.s.i.: an increase of 1300 p.s.i. for 2% addition of tungsten. Addition of only about 0.7% of tantalum to the 4% tungsten-nickel alloy increases the hot strength at about 1600° F. to 6000 p.s.i.; an increase of 1900 p.s.i. for less than 1% addition of tantalum. Furthermore, such increase in the hot strength of a 4% tungsten-nickel alloy requires such large percentage of additional tungsten that the resulting alloy is unsuited for fabrication into cathode sleeves by the usual metal working steps. From a metallographic investigation, it appears that the addition of tungsten and tantalum produces a precipitation hardening effect at intermediate temperatures: however, at cathode-operating temperatures, this effect is quite small and to it cannot be attributed the substantial enhancement of hot strength resulting from small additions of tantalum.

Data compiled on the emission characteristics of indirectly-heated cathodes made of nickel alloys, tungsten-nickel alloys and tungsten-tantalum-nickel alloys indicate interaction of the tungsten and tantalum in enhancement or maintenance of emission characteristics of nickel cathodes, as well as a substantial increase in their resistance to deformation when subjected to severe mechanical shock at cathode-operating temperatures. Such results are not predictable from the prior state of the art. For nickel-cathode alloys containing about 2% to 5% tungsten, by weight, tantalum may be added in the range of about 0.05% to 2% by weight. The tungsten should not be much above 4% because of problems encountered in cathode fabrication. The tantalum should not be much above 0.2% because of coating peel

which would result in a loss of satisfactory emission characteristics. Except for residuals and one or more activating agents, the balance of the alloy is essentially the nickel base usually including cobalt not in excess of 1%: higher percentages of cobalt have been found to have little effect upon the emission characteristics or upon mechanical strength at cathode-operating temperatures.

In these tungsten-tantalum-nickel alloys, magnesium and/or aluminum may be present in small percentages as activating agents. The percentage of magnesium should not be in excess of 0.07% to insure a low rate of sublimation. The percentage of aluminum should not be in excess of about 0.1% to avoid peeling of the oxide coating. Because of its effect upon interface impedance, silicon should not be used as an activating agent; if present, its concentration should not exceed about 0.02%.

In determination of the limits of tungsten and tantalum, for obtaining enhanced hot strength of indirectly-heated cathodes, and preservation or enhancement of emission properties, tests were conducted on several tungsten-tantalum-nickel cathode alloys. Specific examples of such alloys are listed below in Table A.

Table A

Alloy	Ta	W	Al	Mg	Si	Fe	Mn	C	Cu	Co	Ni
#5523----	.08	4.02	.16	.011	.008	.026	.052	.09	.01	4.64	Essentially Remainder.
#5528----	.72	3.79	.115	.017	.008	.021	.097	.01	.012	.182	Do.
#220*----	------	------	.009	.045	.019	.046	.137	.08	.033	.525	Do.

*Reference alloy.

As shown by the test curves of Fig. 1, the yield strengths of the tungsten-tantalum-nickel alloys #5523 and #5528 of Table A are significantly higher than that of the #220 reference-nickel alloy throughout a high temperature range including cathode-operating temperatures in the vicinity of 1600° F. In general, as determined by these and other tests, the hot yield strength of tungsten-nickel alloys may be as much as three times that of the reference-nickel alloy. As confirmed by shock tests on tubes with cathodes at operating temperatures, there is direct correlation between the shock deformation characteristics of indirectly-heated cathodes and the yield strength of the cathode alloy at the same temperatures.

From comparison of the curves of the tungsten-tantalum-nickel alloys #5523 and #5528, it appears that increasing the percentage of tantalum in the ternary alloy significantly increases the yield strength at cathode-operating temperatures.

The higher percentage of cobalt in the #5523 alloy appears to increase the yield strength at temperatures below about 1300° F. but to have little or no effect at temperatures above 1300° F. The presence of cobalt up to 5% or even up to 15% or more is not considered as enhancing the strength, at cathode-operating temperatures, of the alloys here concerned. For this reason and also because of the general shortage of cobalt, it need not be included in or added to the nickel base in amounts of more than 1%.

The addition of a small amount of aluminum, up to not more than about 0.1%, it is desirable but not necessary for early activation of emission. This amount of aluminum has not been found appreciably to affect the yield strength of the tungsten-tantalum-nickel alloys at cathode-operating temperatures, although it may serve to result in precipitation hardening at lower temperatures.

The emission charactermistics of oxide coated cathodes using alloy #5523 of Table A are shown in Figs. 2A, 2B and 3. For these emission tests, the test cathodes and the reference cathodes were utilized in the standard diode structures defined in Spec. F270–52T of ASTM (American Society for Testing Materials). The cathode sleeves were 0.045" O.D. x 0.002" wall x 27 mm. long. The life burning conditions were an anode-cathode supply voltage (E_b) of 100 volts, a heater voltage (E_f) of 6.5 volts and a load resistance (R_b) of 1000 ohms. Anode current readings were taken at 0, 5, 25, 50, 100, 200, 350 and 500 hours and then every 250 hours to the end of the test. At each test period, the anode current was read for a plate voltage of 40 volts for a series of heater voltages including the normal voltage (i.e., 6.5 volts) and sub-normal voltages including 4.5 volts. Such anode current readings plotted against time constitute the curves of Figs. 2A, 2B. The I_sFM or direct-current emission figure of merit curves of Fig. 3 are derived from the anode current vs. heater voltage readings as described in detail in an article of Briggs and Richard in the ASTM Bulletin for January 1951. Briefly, the I_sFM value is the ratio of the I_b, E_f coordinates at the knee of the anode current/heater voltage curve where the anode current changes from a space charge limited condition to a temperature-limited condition (sub-normal heater voltage). For comparison purposes, the emission curves for tubes having nickel cathodes are also shown in Figs. 2A, 2B, 3.

Referring to Figs. 2A, 2B and 3, the cathodes of alloy #5523 activated by 16 hours of life, at which time the FM value was 13.9. The reference #220 alloy cathodes required 23 hours of life to activate, but then had a somewhat higher FM value (14.6). As shown in Fig. 2A, the emission of #5523 alloy cathodes at normal heater voltage fell somewhat during the first 500 hours of life and then stabilized at a value which at 1000 hours of life was somewhat higher than the continuously falling emission of the reference cathodes. As shown in Fig. 2B, the emission of the #5523 alloy cathodes at sub-normal heater voltage rapidly fell during the first 350 hours of life, then fell much more slowly, stabilizing at 750 hours for the rest of the thousand-hour life test. Such decreased emission at sub-normal heater voltage, which also affects the FM curve of Fig. 3, was determined, from examination of the #5523 cathodes after completion of the life test, as being due to peeling of the oxide coating. Such peeling was attributed to excessive percentage of aluminum (0.16%) for this particular alloy. As to their relative sublimation characteristics, the cathodes of the #5523 alloy had only a faint trace of deposit at 1,000 hours, whereas the reference alloy cathodes had a visible deposit at 25 hours and a heavy deposit at 1,000 hours.

In brief summary, tungsten-tantalum-nickel cathodes have an emission characteristic which is stable and substantially equivalent to that of reference-nickel cathodes: their sublimation characteristics are superior to those of reference-nickel cathodes: for good coating adherence and low interface impedance, the tungsten-tantalum-nickel cathode alloys should not contain aluminum in excess of about 0.1% or silicon in excess of 0.02%; tungsten-tantalum-nickel cathodes have a resistance to deformation, which at cathode-operating temperatures, may be one and one-half to three times that of reference-nickel cathodes.

It shall be understood that the term "indirectly-heated cathode structure" used in the following claims includes cathodes, cathode sleeves, cups and the like and excludes directly-heated filamentary cathodes of wire or ribbon.

What is claimed is:

1. An indirectly-heated cathode structure characterized

by enhanced strength at cathode-operating temperatures and by good emission properties and composed of an alloy containing, by weight, 1% to 5% tungsten, .05% to 2% tantalum and the remainder essentially nickel.

2. An indirectly-heated cathode structure characterized by enhanced strength at cathode-operating temperature and with good emission properties and composed of an alloy containing, by weight, tantalum in the range of 0.05% to 2%; tungsten in the range of 1% to 5%; at least one of the activating agents aluminum and magnesium not exceeding the limits of 0.1% aluminum, 0.07% magnesium; and the remainder essentially nickel with not more than 0.1% iron, 0.1% manganese, 0.05% carbon and 0.05% copper as residuals.

3. An indirectly-heated cathode structure characterized by enhanced strength at cathode-operating temperature and with good emission properties and composed of an alloy containing, by weight, about 0.2% tantalum; about 4% tungsten; at least one of the activating agents aluminum and magnesium not exceeding the limits of 0.1% aluminum, 0.07% magnesium, and the remainder essentially nickel with not more than 0.1% iron, 0.1% manganese, 0.05% carbon and 0.05% copper, as residuals.

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