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## METHOD OF MAKING NICKEL-CARBON ALLOY SLEEVES

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The present invention relates to a carbon-nickel alloy, and more particularly to a useful and workable carbon-nickel alloy containing an increased amount of carbon than heretofore feasible, and to a novel and advantageous method of making the alloy.

Nickel alloys have heretofore been used widely for the cores of oxide coated cathodes for electron tubes. Such alloys have generally included carbon and have been made by adding carbon to melts of the elements forming the alloy. The carbon has served two functions in the making of the alloy and in the subsequent use of the alloy as the core for a cathode. One of these functions has been to deoxidize the melt to eliminate oxygen from the final cathode core to prevent poisoning of the cathode. The other function has been to serve as a reducing agent during operation of the cathode, to reduce or activate the electron emitting oxides in the cathode coating for desired emission.

The use of carbon in a nickel alloy has heretofore prevented several serious problems. Alloys of this type have usually been made by adding the carbon to a melt of the alloy. To preserve the hot working quality of the alloy, it has been necessary to limit the amount of carbon added to the melt. It was found, for example, that an excess of 1.0% carbon by weight added to the melt, made the nickel too brittle to hot-work conveniently. As a matter of fact, it was taught in Patent 2,179,110 to Widell that the largest tolerable amount of carbon that could be added to a melt was .50%. This provided from 0.3 to 0.4% carbon in the ingots formed of the melt, and after rolling and annealing, between .03 and .05% carbon remained in the nickel.

The loss of carbon during the rolling and annealing operations referred to, is believed occasioned by the relatively small size of its atoms in relation to the atomic structure of nickel. As a consequence of their small size, the carbon atoms added to the nickel in the melt, diffuse rapidly through the nickel, particularly during hot rolling and annealing of the carbon-nickel alloy at which time much of the carbon is removed from the surface of the alloy. Carbon atoms are smaller in size than the spaces between the nickel atoms. This permits the carbon atoms to move freely through the mass of nickel with little interference from the nickel.

This loss cannot be made up by adding a larger amount of carbon to the melt. This is for the reason that alloys including nickel and a substantial amount of carbon are relatively hard, particularly at the relatively high temperatures required in the forging and rolling of cast or ingot nickel into wire and strip, which are forms required for some electron tube applications such as filamentary cathodes and cathode sleeves. Therefore, it is undesirable to introduce large amounts of carbon into the melt in order to retain carbon in the finished wire or strip.

In view of the foregoing, carbon-nickel alloys of the prior art were confronted by a serious limitation as to the amount of carbon they could contain. As a result

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of this limitation, the prior art found it necessary to add other reducing materials to the alloy, to give the cathode core its required reducing action.

Among such other reducing materials were included silicon and magnesium. However, while each of these materials contributed to increased reduction of the emitting oxides by the cathode core, they are objectionable in that the silicon forms a compound that manifests itself as a high resistance interface between the core and coating that causes peeling of the coating from the core, and in that the fugitive character of the magnesium causes it to form objectionable deposits on tube components.

Some types of commercially available nickel contain magnesium, silicon and titanium. One type includes from 0.02% to 0.04% silicon as a deoxidizer of oxide compounds in the nickel; from 0.03% to 0.05% magnesium for eliminating sulfur; and similar amounts of titanium for improved workability. Another type of nickel used heretofore for cathodes from which high emission is desired, includes as much as 0.20% silicon. While the presence of these elements in the nickel retards the diffusion of carbon therefrom, they are objectionable as indicated before herein.

However, even though the relatively small amounts of silicon and magnesium present in some types of commercial nickel might render the nickel tolerable as the base metal of an alloy for cathodes if sufficient carbon were present to make up for the reduced amount of silicon and magnesium, the carbon required would be greater than that which could be added to the alloy by available methods, as indicated before herein.

While a nickel alloy containing some silicon and magnesium might be tolerable for use in cathodes, an alloy of carbon and nickel only, is preferable, because of an important advantage of carbon as a deoxidizing and activating agent, over silicon and magnesium. This advantage resides in the fact that when carbon deoxidizes nickel or reduces oxygen compounds in the base or core material of a cathode, or reduces the emitting substance of the cathode, such as barium oxide, for securing active barium for emission purposes, it produces the oxide of carbon which is a gas and which escapes from the cathode and is subsequently eliminated by a getter generally used in electron tubes. On the other hand, when conventional deoxidizers are used such as silicon, magnesium and titanium, the combination of these elements with oxygen in the base or core of a cathode and in the oxide of the emitting substance, results in the formation of solid oxides on the cathode, which produce objectionable effects, such as high resistance, which are deleterious to emission. Consequently, the use of an alloy including substantially only carbon and nickel is superior to an alloy also including silicon, magnesium or titanium, when used in cathodes.

Accordingly, it is an object of the present invention to provide a workable carbon-nickel alloy having an increased amount of carbon therein.

A further object is to provide an improved core for a coated cathode.

Another object is to provide a carbon-nickel alloy core for a cathode, in which the carbon in the alloy effectively serves as the sole reducing agent therein.

A further object is to provide a novel method of making a carbon-nickel alloy.

Another object is to provide a method of making a carbon-nickel alloy cathode core wherein the carbon is in an amount to serve as the sole activating agent of the core and wherein the core is formed to desired shape either before or after the addition of the carbon to the alloy.

A further object is to provide a method of making a

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carbon-nickel alloy by diffusing the carbon into the nickel while the latter is in a solid state.

Briefly considered, the invention provides a carbon-nickel alloy that after working and annealing, includes as much as 0.10% carbon by weight. This alloy is well suited for service as the core of an indirectly heated cathode without the addition thereto of further reducing agents. The amount of carbon in the alloy is sufficient for desired reduction of the oxide coating required for good emission. There is, therefore, no need to rely on the more objectionable reducing materials, such as silicon and magnesium.

The novel method of the invention involves heating worked nickel or working the nickel in a carbon bearing gas or vapor for a predetermined time and at a predetermined temperature, to cause the carbon in the gas or vapor to diffuse into the nickel. For best results, the carbon gas or vapor has a predetermined carbon concentration, and the temperature and time referred to are controlled to prevent excessive softening of the alloy and the formation of a surface layer of carbon.

Further objects and advantages of the invention will appear as the present description proceeds.

Alloys of nickel, carbon and other elements, have been used heretofore for the base or core of oxide coated cathodes. Pure nickel does not make a good cathode core material because it has insufficient reducing action for activating the oxide coating. It has not been feasible heretofore to use only one reducing or activating element in the core such as silicon, magnesium, carbon, etc.

Thus silicon, which is a well known reducing agent, forms an objectionable interface between the coating and core when used in an amount to provide, per se, the desired activation. Another element, magnesium, which is also recognized as a reducing material, cannot be used in an amount required for good activation, because of its fugitive character, as a consequence of which it forms objectionable deposits within the tube. Carbon is another recognized reducing material, but here again, it has not been feasible in the prior art to use carbon only in an amount thereof that good activation calls for.

A limitation on the carbon content of the core alloy is imposed by the method followed heretofore in making the alloy. This method has involved melting the nickel and adding the other components of the alloy to the melt. After the melt hardens, it is worked and annealed to reduce its brittleness and to make it suitable for desired forming operations. Carbon has the property of hardening an alloy of which it forms a part. Therefore, the prior art had set a limit as to the amount of carbon to be added to the melt. This limit from a practical standpoint was 0.50% of carbon by weight of the melt. However, during the annealing operation, most of the carbon was lost, leaving only from .005 to .02% carbon in the alloy. This amount of carbon is insufficient when used alone for activation of the emitting oxides required for high electron emission.

According to the invention, a carbon-nickel alloy is provided having up to 0.10% carbon without the disadvantage of reduced workability. This amount of carbon, when used as the sole reducing element of the alloy, is adequate for good emission. The alloy of the invention is made possible by a novel method of making it. According to the method, the alloy is formed while the nickel is in the solid state and involves a diffusion of carbon from the outside into the solid nickel. The nickel may be worked prior to or after the addition of the carbon thereto.

According to one way of practicing the method of the invention, a plurality of formed nickel cathode sleeves are heated for from 15 to 90 minutes at a temperature of from 550° to 700° C. in an atmosphere comprising hydrogen or nitrogen or a mixture thereof containing from 0.1 to 1.0% propane, or other carbonaceous gas or vapor. The sleeves are carried in boats through a furnace having

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the atmosphere referred to and operated at the temperature indicated.

The temperatures of the range referred to are relatively low. This is for the reason that higher temperatures have an undesirable softening effect on the nickel.

The introduction of carbon into nickel by the method of the invention requires a suitable balance between the rate of decomposition of carbonized gas or vapor and the rate of diffusion of the carbon product of this decomposition into the nickel. This balance is produced by a proper selection of time and temperature of the firing operation and the vapor pressure and concentration of the hydrocarbon in the atmosphere referred to, and the rate of decomposition of the hydrocarbon on the surface of the metal being alloyed.

It has been found necessary therefore, to practice the method of the invention at a temperature below 700° C. in order to avoid excessive annealing and softening of the carbon-nickel end product. As a matter of fact, it would be preferable to use temperatures below 550° C. because of the undesirable annealing and softening effects referred to, but it is found that the rate of diffusion of carbon into the nickel is so low at temperatures below 550° C. as to require excessively long periods of firing. Therefore, according to the invention, the lower limit of the temperature range useful in practicing the method is 550° C., and the time duration of the firing step is from 15 to 90 minutes.

The vapor pressure and concentration of the hydrocarbon in the atmosphere to which the nickel is subjected according to the invention, requires careful control in order to avoid a deposit of carbon on the cathode. If the concentration of the hydrocarbon is too high in relation to its decomposition rate determined by the nickel surface, carbon is deposited on the nickel surface at a greater rate than that at which can be absorbed by or diffused into the nickel. The resultant black deposit on the surface of the cathode lowers its temperature as a consequence of the high heat radiation from a black body. This results in undesirable lower emission from the cathode. On the other hand, if the concentration of the hydrocarbon in the carbonaceous atmosphere is too low, a too small an amount of carbon is diffused into the nickel in a given time of reasonable length, at the temperatures referred to. Therefore, according to the invention, the concentration of the hydrocarbon in the firing atmosphere referred to is within a predetermined range. This range is from 0.1 to 1.0% by weight of the atmosphere used.

It is believed that nickel serves as a catalyst for decomposing the hydrocarbon in the carbonaceous atmosphere in which the nickel is fired according to the invention. It appears that a nickel surface is a better catalyst in this connection than the surfaces of ceramics such as aluminum oxide. Copper has little or no efficacy in this respect. It should be noted that at the temperatures used in practicing the method of the invention, the hydrocarbon does not decompose spontaneously in space. Such decomposition is believed to require the catalytic action of a surface such as that of nickel.

This selective decomposition of carbon on surfaces of different materials is of value in practicing the invention. For example, the nickel into which the carbon is to be diffused, may be carried in boats made of copper, and the furnace used may have a lining of aluminum oxide. This assures deposition of the carbon on the nickel only, the copper boats and furnace lining being free from such deposition.

It should be noted in this connection that the addition of the carbon to the nickel results in some hardening thereof. This hardening effect, however, compensates for any softening effects that the temperatures used, according to the invention, have on the alloy. The combined effect of the added carbon to the nickel and the heating of the nickel to cause carbon diffusion thereto is therefore to leave the resultant alloy in about the same

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condition with respect to ductility and softness as characterized the original nickel.

The method of the invention provides a novel means for determining the duration of the heat treatment referred to for processing nickel sleeves so as to have up to 0.1% carbon. According to this means, a nickel strip is placed in one or more boats with the nickel sleeves or work pieces, and its electrical resistance is measured during the firing operation. It has been found that if the resistance of the strip increases by from 10 to 25%, the sleeves in the boats are properly processed and contain from .04 to 0.10% carbon. As an alternative, the resistance of the sleeves themselves may be measured to determine the duration of the heat treatment.

As alternatives to propane referred to before herein, the carbonizing atmosphere may contain methane, ethane, or other hydrocarbon gases, or vapors such as isopropyl alcohol, methanol, ethyl alcohol, propyl alcohol (benzol, benzene, gasoline) and the like. The amounts of these gases or vapors should be from 0.1 to 1.0% of the atmosphere use, as in the case of propane above referred to.

The use of isopropyl alcohol is preferred, since it has a lesser tendency to form an objectionable carbon surface, than the other carbon bearing media referred to.

One way of forming the atmosphere with the required amount of carbon therein, is to pass the hydrogen or nitrogen or mixture of both, over the particular liquid such as methanol, or benzene to obtain the vapor desired. When the carbon is included in a gas, the gas in the relative amount indicated is fed to the hydrogen-nitrogen atmosphere.

Instead of subjecting the formed sleeve to the carbon diffusion operation of the invention, it is also possible according to the invention to introduce the carbon into the strip or tubing from which the sleeves are to be made. This can be done during the final annealing of the strip or tubing by introducing the carbonaceous gas or vapor into the hydrogen atmosphere used during such annealing operation. This is more advantageous than dealing with finished sleeves, since it avoids the danger of deformation of the formed sleeve during the carbon diffusion operation, such as might occur on a careless placement or arrangement of the sleeves in the boats referred to.

According to a specific example, cathode sleeves were heated in an atmosphere of hydrogen that had been passed over isopropyl alcohol to provide a concentration of hydrocarbon gas of about 0.5%. The sleeves were carried in copper boats through a furnace containing said atmosphere and operated at about 600° C. and remained in the furnace for 55 minutes. The furnace was provided with a lining of aluminum oxide. The boats also contained strips of nickel for the resistance measurements referred to. It was found that after 55 minutes, a resistance measurement of the strips indicated an increase in resistance of about 12%. A quantitative analysis of the resultant metal and carbon alloy showed the alloy to contain 0.06% carbon.

Cathode sleeves treated in the foregoing manner showed remarkable performance. When such sleeves were included in electron tubes known commercially by type 12AU7, it was possible to get low voltage mutual conductance of from 3000 to 3200, whereas when sleeves of prior art nickel alloys were used, a conductance of only

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1500 to 2000 was obtained. Sleeves made of the alloy of the invention were also tried in tubes commercially known as type 6AK5. The conduction of such tubes was from 5000 to 5500 even after 500 hours of life.

5 Tubes of this type using sleeves not treated according to the invention had a conductance of only 3000 to 4000.

It is apparent from the foregoing that a novel and advantageous nickel-carbon alloy for use as cathode core is provided by the invention. The alloy includes more carbon than feasible heretofore in nickel alloys without sacrifice of ductility, and as a consequence the carbon content may be included in a sufficient amount to serve as the sole activating material in the core, thus making unnecessary the use of other activating agents such as silicon and magnesium which are objectionable as indicated before herein. The invention also provides a novel method of making a nickel-carbon alloy, by diffusing the carbon into the nickel from the outside thereof, as distinct from including the carbon in a melt of nickel. The method also provides a novel way for determining the proper concentration of carbon in the alloy to afford assurance against adding an excessive and coating-forming amount of carbon thereto.

What is claimed is:

1. Method of making a high carbon content alloy-nickel sleeve for a coated cathode, comprising the steps of forming said sleeve of substantially pure nickel sheet metal, heating said sleeve and a strip of nickel in a furnace containing from 0.1% to 1.0% of a carbon bearing medium consisting of at least one of propane, methane, ethane, methanol, ethyl alcohol, propyl alcohol, isopropyl alcohol, benzol, benzene and gasoline, at a temperature below 700° C. to prevent excessive softening of said sleeve and to diffuse carbon into the nickel of said sleeve and strip at a rate to prevent formation of a carbon coating on said sleeve, measuring the resistance of said strip of nickel during said heating step, and stopping said heating step when said resistance is from 10 to 25% higher than prior to said heating step, whereby said sleeve contains from 0.04 to 0.10% carbon by weight without an objectionable outer coating of carbon.

2. Method of making a ductile, high carbon content carbon-nickel alloy sleeve for a coated cathode, comprising the steps of heating a nickel work piece in an atmosphere containing from 0.1% to 1.0% isopropyl alcohol at a temperature from 550° C. to 700° C. for from 15 to 90 minutes to diffuse from 0.04 to 0.10% by weight of carbon into said nickel at a rate to prevent formation of a carbon coating on said work piece, and forming said work piece when cool to sleeve shape.

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