Aug. 25, 1936. W. F. DESTER 2,051,828

METHOD OF MAKING CARBONIZED NICKEL AND NICKEL ALLOYS

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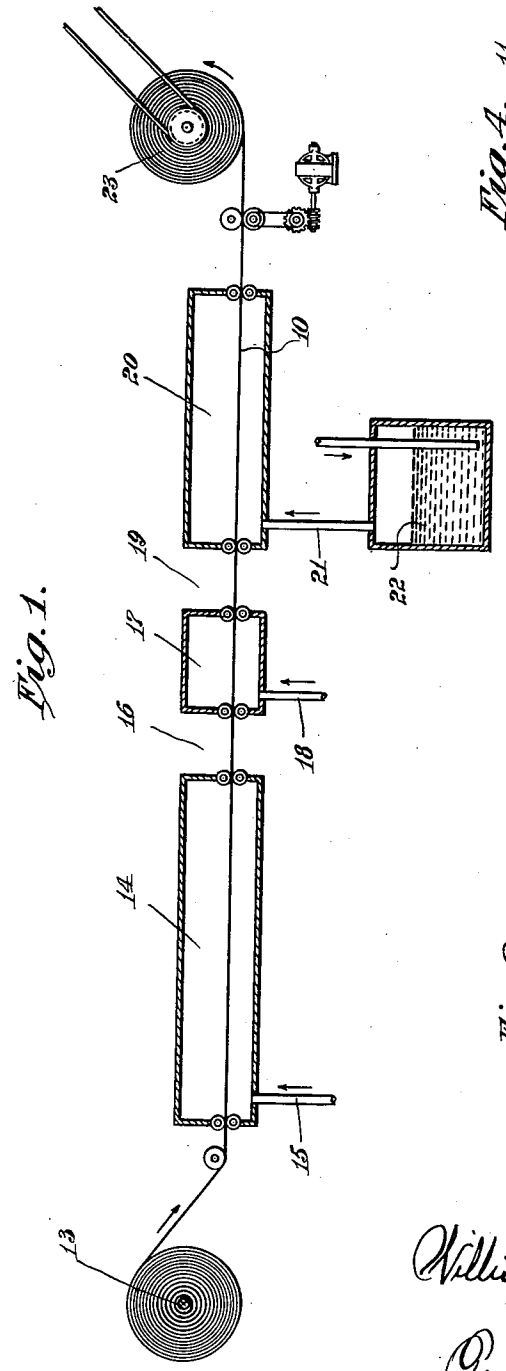


Fig. 1.

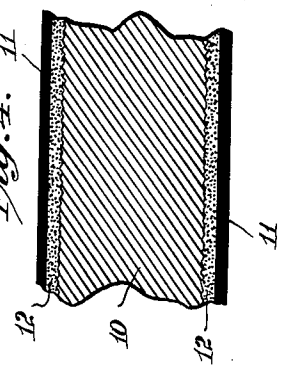


Fig. 4.

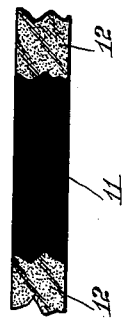


Fig. 3.

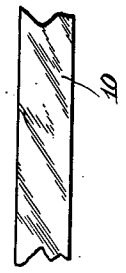


Fig. 2.

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METHOD OF MAKING CARBONIZED NICKEL AND NICKEL ALLOYS

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6 Claims. (Cl. 148—17)

The invention relates to carbonized nickel and nickel alloys and the method of making same, and more particularly to a strand or strip of nickel or a nickel alloy consisting of a malleable base having a carbonized surface, and to the method of producing same by a continuing process.

It is generally recognized that the efficiency of the elements of an audion tube is increased if the surface of the metal of these elements is dulled so as to increase the absorption of heat by the elements and avoid the reflection of light rays thereby. It is also a generally accepted theory that the use of a darkened or carbon coated metal in the elements also modifies the action of the electrons.

Prior to my invention, it has been proposed to produce a strip of nickel or nickel alloy for use in making the elements of audion tubes, wherein the dulling of the surface of the strip is secured by forming a nickel oxide upon the surface of said strip, or by depositing carbon upon the surface of the strip in the presence of an elevated temperature.

It has been found, in actual practice, that with a strip having a nickel oxide upon the surface, deterioration of an audion tube is rapid, due to the reactions which occur upon the heating of the tube while in use.

In a nickel or nickel alloy strip having a carbonized surface, it has been found that the carbon is lightly and irregularly bonded to the base and develops a polish or sheen during the finishing operation of the strip and during the forming of the strip material to produce the plates or grids for use in audion tubes.

Furthermore, the base material, before oxidation, or before being carbonized, presents a granular or lightly pitted surface, and the coating of oxide or carbon follows the contour of the surface irregularities of the base strip, which it is believed varies the electronic action of a tube while it is in use.

With the above conditions in mind, I have produced a carbonized nickel or nickel alloy in strand or strip form, the surface of which has a coating of carbon which is firmly bonded to the metal base by an intermediate stratum of the reaction products of a reduced oxide of nickel in the presence of carbon combined with the metal of the base by carburizing. This intermediate stratum reduces or fills surface pits or other irregularities therein, is permanently bonded mechanically and chemically to the base of nickel or nickel alloy and has a strong affinity for carbon so that during the finishing operation for the removal of surplus or free carbon, and when drawing the carbonized strand or strip to give it the desired form for use in audion tubes, there is no tendency toward the development of a polish or sheen, nor toward the separation of the carbon to a substantial extent, from the base. The material, at the surface thereof, is not materially harder than the metal or alloy base itself, and this surface is substantially free from those pits and irregularities inherent to the base metal or alloy and developed during the drawing operation in producing such strands or strips.

The material may be drawn by means of dies and handled during the assembling of the parts for an audion tube without dislodgment of the carbon upon surfaces of the material and without developing a material gloss or sheen upon such surfaces.

The carbonized nickel or nickel alloy may be produced by succeeding steps of a continuous process permitting controlled time intervals and temperatures during the succeeding stages of the method. The method may be practiced with a considerable temperature range, but any temperature variation must be accompanied by a variation in the time interval. While in the method of the invention, air or water quenching may be resorted to, this is solely for the purpose of permitting the desired temperature variation in the succeeding stages.

The invention consists primarily in the herein described method of producing carbonized nickel or nickel alloy in strand or strip form, consisting in subjecting the strand or strip to an elevated temperature in the presence of a hydro-carbon gas, thereafter subjecting it to an elevated temperature in the presence of an oxidizing agent, and then subjecting it to an elevated temperature in the presence of a hydro-carbon gas, all as are hereinafter set forth and described and more particularly pointed out in the claims hereto appended.

Referring to the drawing,

Fig. 1 is a diagrammatic showing of the method of the invention;

Fig. 2 is a view of a strip before being subjected to the method of the invention;

Fig. 3 is a section of the completed strip with a portion of the carbonized surface removed to disclose the intermediate stratum; and

Fig. 4 is a cross section of a strip upon a greatly enlarged scale.

Like numerals refer to like parts throughout the several views.

The strand or strip material of the invention comprises a base 10 of nickel or nickel alloy such as nichrome having a carbonized outer stratum 11 and an intermediate stratum 12 of the reaction products of reduced oxide of nickel in the presence of carbon.

The intermediate stratum 12 is chemically and mechanically bonded to the surface of the base 10, and the outer stratum 11 is combined with the intermediate stratum so as to be firmly anchored to the base 10 through the medium of this intermediate stratum. In fact, this outer stratum is so firmly bonded to the base and the intermediate stratum that the carbon particles cannot be dislodged by the ordinary processes followed in the production of the elements for audion tubes.

Said stratum 12 has a dull, black, lusterless surface having a substantially uniform density of color throughout. It is also substantially even and smooth upon its outer surface being free from small pits or interstices due to pits or other irregularities in the surface of the base 10 or to the dislodgment of free carbon from the surface of the strand or strip.

By reason of the uniformity and the density of the blackness of the surface of the strand or strip material and the absence of exposed minute portions of the surface of the base 10, the material has high absorptive properties.

Because of the firm bonding or combining of the carbonized surface to the base, it is possible for audion tube elements made therefrom to have substantially the same surface characteristics resulting in greater uniformity in the action of different tubes including such elements, than is possible where the surface characteristics of the elements in different tubes vary.

The efficiency of the tubes is also increased because of the absence of certain surface irregularities in the elements of the tube.

In the practice of the method of my invention used in the production of a carbonized strand or strip of nickel or nickel alloy having the characteristics above referred to, the first step is to carburize the strip. This step is followed by a reduction of the carburized surface, and the final step is a carbonizing of the strip. These three operations are carried on in succeeding stages during a slow travel of a strand or strip from a supply reel to a rewind reel, the temperature in the different stages varying and the rate of traverse of a strip or strand being determined by the time interval required to secure the desired conditioning of the surface as determined by the temperatures to which the strand or strip is subjected during each stage of the method.

In Fig. 1 of the drawing, I have shown conventionally the agencies used at the three stages. At 13, I have shown a supply reel of a strip of nickel or nickel alloy such as is shown in Fig. 2. From the reel 13, the strip passes through a carburizing furnace 14 to which a hydro-carbon gas is introduced through the pipe 15. A temperature range of from 1400° to 2300° F. is maintained within this furnace. The furnace itself is approximately eleven feet long and the rate of travel of the strand or strip will vary from three inches to one foot per minute according to whether the operative temperature is toward the minimum or the maximum within the temperature range stated. With a temperature of about 1400° F., the time interval during which the strand or strip will be passing through the carburizing stage will, therefore, be approximately three quarters of an hour. While with the higher temperature 2300° F., the time interval will be approximately ten minutes. During its passage through the furnace 14, the expansion of the metal permits a penetration of carbon from the decomposed hydro-carbon gas, into such voids, thus firmly embedding carbon particles in this surface while combining carbon with the material of the strip or strand.

Upon leaving the furnace 14, the strand or strip with its carburized surface passes an air gap shown at 16 and enters the furnace 17 at the second or reduction stage. This furnace is maintained at a temperature of from 1750° to 2000° F. and is charged with an atmosphere of oxygen or similar de-carburizing agent which is delivered within the furnace through the pipe 18. The length of this furnace is approximately three feet, thus affording a time interval of from twelve to three minutes according to whether the operative temperature is toward the minimum or the maximum within the range stated.

Upon leaving the de-carburizing stage, the strand or strip is passed through a gap 19 and enters the carbonizing chamber 20, which is maintained at a temperature of from 1000° to 1500° F. Hydro-carbon gas is delivered to the carbonizing furnace 20 through the pipe 21. If desired, this gas may be enriched before delivery to the furnace 20 by passing it through a tank 22 containing a liquid hydro-carbon such as gasolene, kerosene or crude oil. The furnace 20 is approximately eight feet long, thus affording a time interval of from about half an hour to eight minutes according to whether the temperature is toward the minimum or the maximum temperature within the range stated.

After leaving the furnace 20, the strand or strip is wound upon a rewind reel shown at 23, and after cooling, it is subjected to a final finishing operation, which consists merely in a wiping operation by an ordinary cloth to remove any carbon upon the strand or strip which is not sufficiently bonded to the surface produced in the carburizing and the reducing stages of the method.

In the practice of the method of my invention, I have gotten highly satisfactory results at temperatures and with time intervals approximately midway of the range stated, and have been able to completely carbonize the strand or strip material in from about forty-five minutes to an hour. For the air gaps 16 and 19, which are of a nature to secure an air quenching of the strand or strip, I may substitute a quenching bath as to either or both since the purpose of these gaps is merely to permit the desired variation of the temperatures to which the strand or strip is subjected in the different stages of the method. Such quenching, whether air or water is used, has no effect upon the character of the surface produced, being as stated mere temperature control expedients.

Upon entering the furnace 14, the strand or strip is a bright steel gray; upon entering the de-carburizing furnace 17, the color is a dull steel gray, and upon leaving the de-carburizing furnace and when entering the carbonizing furnace, the color is a greenish gray due to the presence of oxide of nickel.

Upon leaving the carbonizing furnace, the strip is a dull, lusterless, jet black. While within the carburizing furnace, the surface irregularities or minute pits are substantially filled with the

carbon incorporated in the material of the strand or strip and free carbon is deposited throughout the entire surface. While within the de-carburizing furnace, much of the free carbon is eliminated and a nickel oxide is formed upon any portions of the surface which are not thoroughly protected by the carbon, and reactions are set up which will cause a firm chemical bond between the carbon and the nickel or nickel alloy of the base. In the carbonizing stage, the nickel oxide upon the surface is reduced and acts upon the carbon deposited during this stage to combine it with the remaining reaction products of the reduction stage, driving out any oxygen which is freed during the reaction in the carbonizing stage.

Within the temperature range to which the strand or strip is subjected while in the carburizing furnace and with the time interval stated, there is no substantial hardening of the surface of the strand or strip, and this is also true as to the other stages of the method. Consequently, the finished product may be readily drawn to any desired form without the formation of cracks in the surface of the material. The firm bond between the carbon and the metal base avoids possibility of surface flecking during such drawing operations.

The carbonized surface is so hard and so firmly anchored or bonded to the metal of the base that it can be removed only by severe abrasion, so that in the handling of articles made from such strands or strips, there is no possibility of the carbon deposit being dislodged to an extent to form pits or isolated bright areas as a result of the exposure of the base metal through the outer strata. This condition also improves the conductivity of elements made from the strand or strip.

The carbon combined with the nickel during the carburizing stage has an affinity for the carbon deposited during the carbonizing stage, and the reduction of the oxide of nickel during the carbonizing stage results in an effective combining of the carbon deposited during this stage throughout the entire surface of the strand or strip. After the removal of the surplus or free carbon by wiping, practically all of the carbon remaining upon the surface of the strip is firmly bonded or anchored to the nickel or nickel alloy base, and this surface is a smooth continuous surface having substantially uniform color and properties throughout. There are no material pits or irregularities in this surface and none of the metal of the base is exposed.

During the production of an audion tube, or while such tube is in use, the temperatures to which elements made of the material produced by the method of the invention, are subjected, will not cause any change in the condition of the surface of the element, or result in any reaction which will impair the quality of the audion tube or modify the electronic action.

The gases used may be natural gas, methane, butane, a specially prepared gas known commercially as "Pyrofax" or any other hydro-carbon commonly used for carbonizing purposes.

It is not my intention to limit the invention to any exact temperatures or exact time intervals, those stated being the actual temperatures and time intervals which have been used in the commercial production of the carbonized strand or strip.

I believe it to be broadly new to carbonize a nickel or a nickel alloy base by a method involving the three steps in succeeding stages, carburizing the nickel or nickel alloy, oxidizing the carburized material and in the final stage carbonizing the nickel with the incidental reduction of the nickel oxide.

Having described the invention, what I claim as new and desire to have protected by Letters Patent, is:—

1. The herein described method of producing carbonized nickel or nickel alloy in strand or strip form, consisting in subjecting the strand or strip to an elevated temperature in the presence of a hydro-carbon gas, thereafter subjecting it to an elevated temperature in the presence of an oxidizing agent, and then subjecting it to an elevated temperature in the presence of a hydro-carbon gas.

2. The herein described method of producing carbonized nickel or nickel alloy in strand or strip form, consisting in the steps of carburizing the surface of the strip or strand, thereafter forming nickel oxide upon the surface thereof by subjecting the strand or strip to an elevated temperature in the presence of oxygen, and then reducing the nickel oxide by subjecting the strand or strip to an elevated temperature in the presence of a hydro-carbon gas.

3. The herein described method of producing carbonized nickel or nickel alloy in strand or strip form, consisting in subjecting the strand or strip to an elevated temperature for a predetermined time interval in the presence of a hydro-carbon gas to effect carburization of the surface of the strip or strand, thereafter subjecting the strip or strand to an elevated temperature for a predetermined time interval in the presence of an oxidizing agent to form a nickel oxide upon the surface thereof, and then subjecting it to an elevated temperature for a predetermined time interval in the presence of a hydro-carbon gas to reduce the nickel oxide and form a carbonized surface firmly bonded to the strip or strand, the maximum temperature during oxidation being relatively lower and the time interval being relatively shorter than when carburizing, and the temperature during carbonization and the reduction of the nickel oxide being relatively lower and the time interval being relatively longer than during oxidation.

4. The herein described method of producing carbonized nickel or nickel alloy in strand or strip form, consisting in subjecting the strand or strip to a temperature of from 1400° to 2300° F. for from forty-five to ten minutes in the presence of a hydro-carbon gas, thereafter subjecting the strip or strand to a temperature of from 1750° to 2000° F. for from twelve to three minutes in the presence of an oxidizing agent, and then subjecting it to a temperature of from 1000° to 1500° F. for from thirty to eight minutes in the presence of a hydro-carbon gas.

5. The herein described method of producing carbonized nickel or nickel alloy in strand or strip form, consisting in imparting continuing movement to a strip or strand to successively subject it to an elevated temperature in the presence of a hydro-carbon gas, to a quenching medium, to an elevated temperature in the presence of an oxidizing agent, to a second quenching medium, and then to an elevated temperature in the presence of a hydro-carbon gas.

6. The herein described method of producing carbonized nickel or nickel alloy in strand or

strip form, consisting in imparting continuing movement to a strip or strand to successively subject it to a temperature of from 1400° to 2300° F. for from forty-five to ten minutes in the presence of a hydro-carbon gas, to a quenching medium, to a temperature of from 1750° to 2000° F. for from twelve to three minutes in the presence of an oxidizing agent, to a second quenching medium, and then to a temperature of from 1000° to 1500° F. for from thirty to eight minutes in the presence of a hydro-carbon gas.

WILLIAM F. DESTER.