Aug. 19, 1941. P. R. KALISCHER 2,253,334

PROCESS FOR TREATING NICKEL-BEARING ALLOYS

Filed Sept. 16, 1937 2 Sheets-Sheet 1

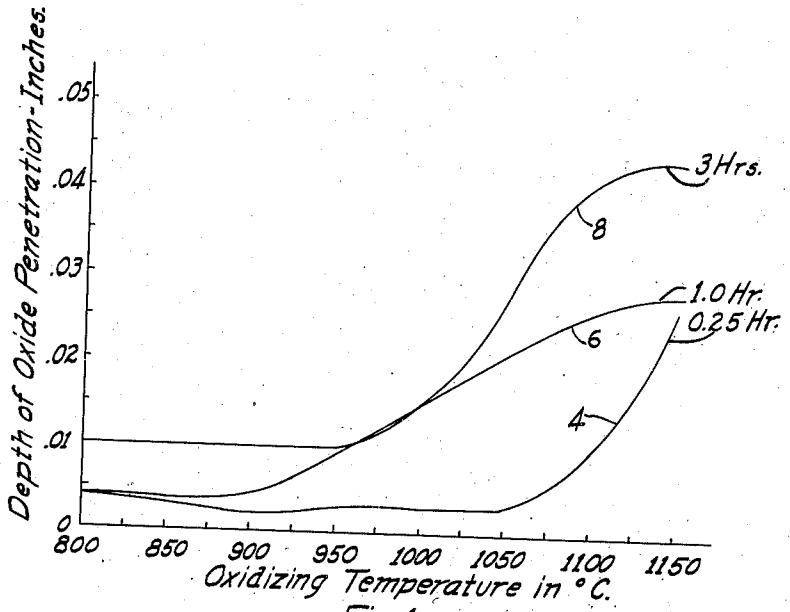

Fig. 1.

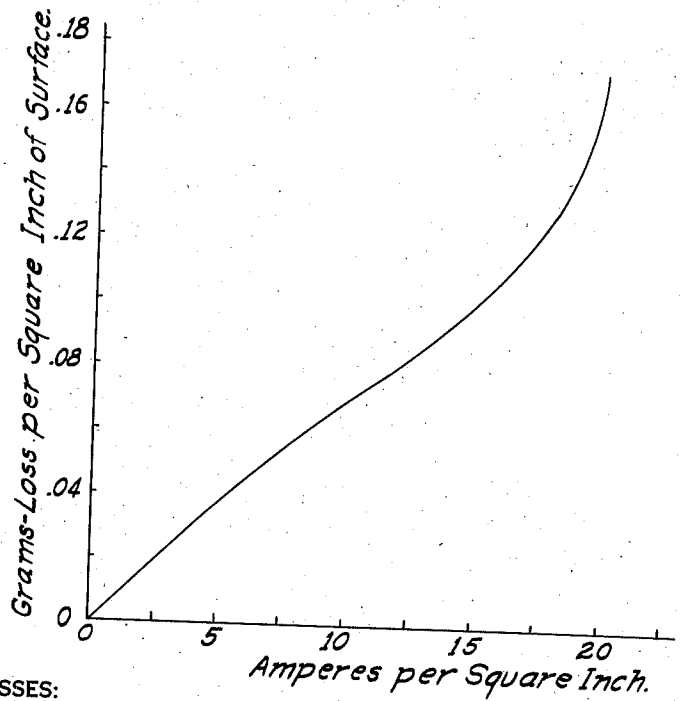

Fig. 2.

WITNESSES:

Leon M. Garman

James K. Ely

INVENTOR

Philip R. Kalischer.

BY

Ezra D. Savage

ATTORNEY

Aug. 19, 1941. P. R. KALISCHER 2,253,334

PROCESS FOR TREATING NICKEL-BEARING ALLOYS

Filed Sept. 16, 1937 2 Sheets-Sheet 2

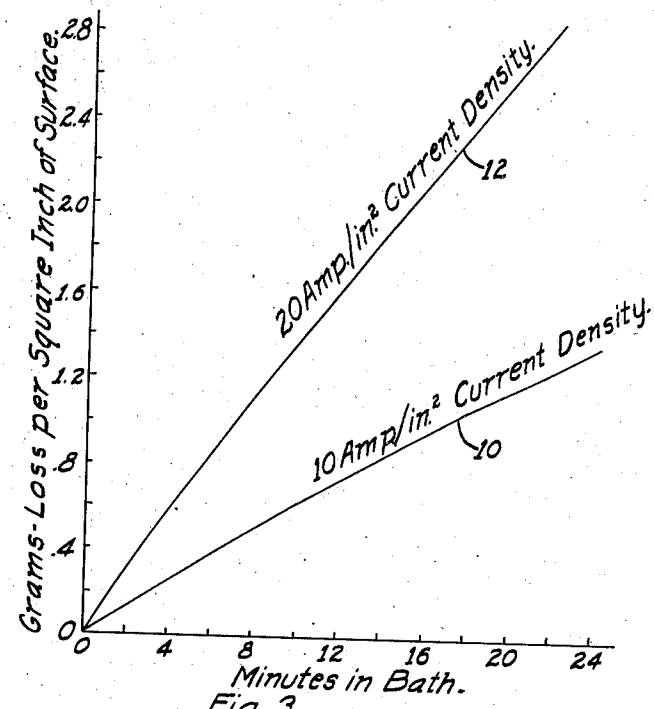

Fig. 3.

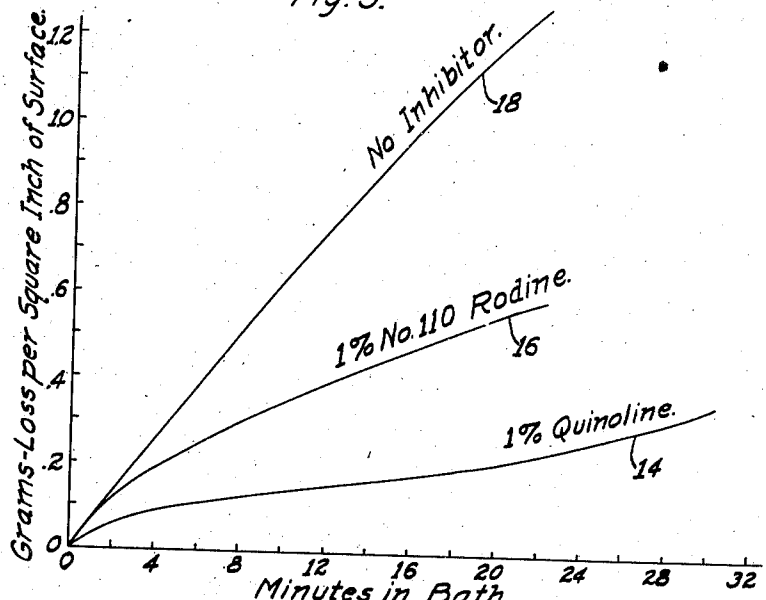

Fig. 4.

WITNESSES:
Leon M. Garman
James M. Daly

INVENTOR
Philip R. Kalischer.
BY
Ezra W. Savage
ATTORNEY

Patented Aug. 19, 1941

2,253,334

UNITED STATES PATENT OFFICE

2,253,334

PROCESS FOR TREATING NICKEL-BEARING ALLOYS

Philip R. Kalischer, Wilkinsburg, Pa., assignor to Westinghouse Electric & Manufacturing Company, East Pittsburgh, Pa., a corporation of Pennsylvania

Application September 16, 1937, Serial No. 164,148

3 Claims. (Cl. 204—145)

This invention relates to the treating of nickel-bearing alloys and particularly to the process for removing surface metal from nickel-bearing alloys.

In fabricating nickel-bearing alloys they are usually subjected to a hot working. The hot working contaminates the alloys treated in that the surface of the alloy is oxidized and upon examination it is found that there is a large amount of intergranular oxidation. This intergranular oxidation is the result of the penetration of oxides along the grain boundaries of the metal at a rate faster than through the body of the crystals of the metal. It is essential that these oxides be removed to produce metal having a clean, smooth, velvety surface. It is also desirable that a surface layer of the metal be removed in order to insure the removal of the intergranular oxides.

In the prior practice, attempts have been made to remove the rough, irregular, damaged metal by machining, chipping, grinding or pickling the metal. The machining, chipping and grinding methods have not proven to be commercially feasible in the case of hot rolled strips and bars, since such methods entail slow, expensive and precise machinery operations.

The pickling methods of the prior practice are also objectionable in that no control can be exercised over the rate of solution of the nickel-bearing alloy in the acid bath. Further, the time element involved in pickling the nickel-bearing alloys is long, requiring an immersion in a hot acid bath for a number of hours to remove the oxides. Such pickling also results in pitting the alloy because of the unequal rate of attack of the acid on the surface thereof.

An object of this invention is to provide for removing oxide film and intergranular oxidation from nickel-bearing alloys.

Another object of this invention is to provide a process whereby nickel-bearing alloys may be treated for removing the oxide film and intergranular oxidation, together with a predetermined amount of the surface metal in a comparatively short period of time thereby producing a clean, smooth and velvety surface on the alloy.

A further object of this invention is to provide for removing surface metal from nickel-bearing alloys by subjecting the alloys to an alternating current in a cold electrolyte.

A more specific object of this invention is to provide for removing a surface layer from alloys containing nickel by treating the alloys in a cold dilute acid bath using an alternating current of low voltage and high current density and an inhibitor to retard solution of the alloy in the acid bath.

Other objects of this invention will become apparent from the following description when taken in conjunction with the accompanying drawings, in which:

Figure 1 is a graph, the curves of which illustrate the effect of different oxidizing temperatures for different periods of time on the depth of the oxide penetration in a representative nickel-bearing alloy;

Fig. 2 is a graph, the curve of which illustrates the effect of different current densities on the weight of a representative material treated in accordance with this invention;

Fig. 3 is a graph, the curves of which illustrate the effect of time of subjecting the representative material to different current densities on the rate of solution of the metal in accordance with this invention; and

Fig. 4 is a graph, the curves of which illustrate the effect of an inhibitor on the rate of solution when treating a representative material in accordance with this invention.

In fabricating the nickel-bearing alloys, the hot working to which they are subjected causes a superficial oxidation of the surface of the alloy with an accompanying intergranular oxidation. The depth of the oxide on the alloy resulting from working the alloy in oxidizing atmospheres at the high temperatures may be easily calculated or measured for any given nickel-bearing alloy.

Referring to the drawings, Fig. 1 thereof illustrates the effect of heating the alloy without an accompanying deformation of different temperatures in an oxidizing atmosphere on the surface of a particular alloy for different periods of time of exposure. In the figure, the abscissa represents the oxidizing temperature and the ordinate represents the depth of the oxide penetration, while curves 4, 6 and 8 represent exposures or treatments for .25 hour, one hour, and three hours, respectively. The particular alloy employed for this illustration is one known to the trade as "Kovar" and comprises 29% nickel and about 17% cobalt in an iron base as covered in Patent No. 1,942,260, issued January 2, 1934, to Howard Scott. Other nickel-bearing alloys, however, react to the hot working in the same manner as the Kovar, which is employed for illustrative purposes.

The depth of the oxide penetration illustrated in Fig. 1, comprises a combination of the superficial and intergranular oxidation, the superficial oxidation being measured by means of a mi-

crometer and the depth of the intergranular oxidation being measured by some suitable microscopic means. The following table sets forth the different measurements upon which the curves of Fig. 1 are based:

Table

Temp. of oxidation, degrees C.	Depth of oxide penetration								
	¼ hr. in furnace			1 hr. in furnace			3 hrs. in furnace		
	Superficial	Intergranular	Total	Superficial	Intergranular	Total	Superficial	Intergranular	Total
800	.004	.000	.004″	.004	.000	.004″	.010	.000	.010″
850	.003	.000	.003	.003	.000	.003	.005	.000	.005
900	.002	.000	.002	.004	.000	.004	.011	.000	.011
950	.003	.000	.003	.006	.003	.009	.010	.000	.010
1000	.003	.000	.003	.006	.000	.006	.015	.000	.015
1050	.003	.000	.003	.014	.007	.021	.027	.000	.027
1100	.007	.003	.010	.014	.003	.017	.029	.012	.041
1150	.013	.013	.026	.017	.012	.029	.030	.014	.044

An examination of these measurements as embodied in the curves of Fig. 1 reveals that the penetration of the intergranular oxidation is not serious unless the nickel-bearing alloy is heated in the oxidizing atmospheres at temperatures above about 1050° C. This temperature may vary somewhat depending upon the alloy treated. However, forging and hot rolling of the nickel-bearing alloys must be done at temperatures of 1100° C. and higher, so that intergranular oxidation is found in the different hot worked alloys. Where the alloy is deformed at these high temperatures, the penetration of the oxide is much more rapid and to a greater depth than illustrated for the alloy that is not hot deformed.

In order to remove a surface layer of the nickel-bearing alloy and thereby remove the oxides which are necessarily present in irregular shapes depending somewhat on the grain boundaries before further fabricating the alloys into a semi-finished shape as by cold working, the hot worked alloy may be subjected to the action of an alternating current of low voltage and high current density in a cold dilute electrolyte. By subjecting the alloy to alternating current, it is found that the time necessary for removing the surface layer of the nickel-bearing alloy containing the intergranular oxides is a matter of minutes and that the rate of solution of the nickel-bearing alloy may be so easily controlled that any predetermined amount of the metal may be removed. In the preferred treatment of the nickel-bearing alloy to remove the surface layer thereof, the alloy is made one of the electrodes.

In practicing this process, it is found that the concentration of the acid bath is relatively unimportant as long as an electrolyte exists. Further, the temperature of the bath need not be high but instead may be maintained as low as possible. In practice, a 5 to 20% solution of cold dilute sulphuric acid is satisfactory as the electrolyte. Other cold dilute baths of electrolyte may, however, be employed.

In order to remove the surface layer of metal, the nickel-bearing alloy may be connected as an electrode in a low voltage circuit which is connected to a suitable source of current, not shown, and immersed in a cold dilute acid bath. With the nickel-bearing alloy employed as one of the electrodes, a graphite rod may be employed as the other or since the current utilized is an alternating current both electrodes may be readily be composed of the nickel-bearing alloy which is to be treated.

Referring to Fig. 2 of the drawings, the curve thereof represents a relation between the loss in weight per square inch of the particular Kovar alloy identified hereinbefore when subjected to different current densities. From this curve, it is evident that by controlling the current density to which the alloy is subjected in the cold dilute acid bath, a predetermined amount of the metal may be removed from the alloy electrode.

Curves 10 and 12 of Fig. 3 further illustrate the effect of time of exposure to the alternating current on the material lost at current densities of 10 amperes per square inch and 20 amperes per square inch, respectively. From these curves, it is found that the rate of solution in the cold dilute acid bath when subjected to the alternating current is proportional to both the time of exposure and the current density. Similar data may be found experimentally for different current densities. Although these curves are based on the Kovar alloy identified hereinbefore, similar curves illustrating this particular relationship between the rate of solution and the time of exposure at different current densities may be readily determined for other nickel-bearing alloys.

Since the rate of attack or the rate of solution of the metal when subjected to the low voltage alternating current having a high current density is more rapid at the grain boundaries of the alloy than on the superficial oxides, it is necessary to provide for retarding the rate of solution to prevent excessive loss of material. It is found that an inhibitor such as quinoline or the compound identified to the trade as No. 110 Rodine, is quite effective in retarding the solution of metal. Where 1% by weight of the inhibitor is employed in the acid bath, it is found that the treated nickel-bearing alloy is provided with the desired clean, satin or velvety finish.

The effect of the inhibitor on retarding the rate of solution is clearly illustrated by curves 14, 16 and 18 of Fig. 4 of the drawings. These curves illustrate the weight of material lost or the rate of solution of metal when subjected to an alternating current having a constant current density of 10 amperes per square inch and a voltage of 12 volts for different periods of time, curve 14 being based upon the use of 1% by weight of quinoline in the electrolyte, curve 16 on the use of 1% by weight of No. 110 Rodine in the electrolyte, and curve 18 upon the use of the cold dilute electrolyte free from an inhibitor.

As the nickel-bearing alloy is withdrawn from the dilute acid bath, it carries a surface film of the acid. In order to remove or neutralize the acid adhering to the surface, the alloy is then dipped in a suitable neutralizing bath such as a lime solution.

Since the solution of the metal when subjected to the treatment as hereinbefore described

starts and proceeds most rapidly at sharp edges, this process is of special value in that it picks out and brings into sharp relief any flaws such as laps, fish scale and fins formed during the working of the metal. By subjecting the hot worked material to an alternating current having a voltage of from 2 to 15 volts and a current density of about 10 amperes per square inch in a cold dilute acid bath, it is found that the metal may be completely cleansed in from 4 to 30 minutes. Further, by means of this process, it is possible to remove predetermined amounts of the surface metal in the cold condition without danger of contaminating the metals by reason of the formation of oxides.

As it is sometimes desired to draw the nickel-bearing alloys such as Kovar into wire, it will be evident that the process of this invention facilitates such fabrication of the metal. This may be readily accomplished by subjecting the hot rolled stock of nickel-bearing metal to the treatment described hereinbefore to free it of the surface layer containing the intergranular oxides and then subjecting it to a cold drawing to reduce it in diameter. By repeatedly subjecting the nickel-bearing alloy to the action of the alternating current and the cold drawing, the stock may be reduced to the desired size of the wire, producing sound, clean wire. This is because the laps and channels present as defects in the surface of the stock after the original treatment were so reduced in size and gradually filled with sound metal during the cold working as to produce sound metal. In practice, the reduction per pass is preferred not to exceed 40% reduction in cross sectional area followed by the alternating current treatment in the acid bath in order to insure complete removal of all intergranular oxides.

Although this invention has been described with reference to a particular nickel-bearing alloy, it has been successfully applied to other nickel-bearing alloys for removing predetermined surface layers therefrom both in the oxidized and unoxidized condition. It has also been successfully employed in removing seams and laps formed on the alloys during rolling processes and scale resulting from heat treatment and other causes. Some of the nickel-bearing alloys treated successfully by this process are those known to the trade as Hypernik, Konal, Nicrome IV, Cromax, Monel metal, stainless steel and others. These alloys and the Kovar referred to hereinbefore are of the group of nickel-iron base alloys in which the nickel plus iron content constitutes the predominating alloying constituents which can be successfully treated by the process of this invention. This invention is, therefore, not to be limited except insofar as is necessitated by the prior art and the scope of the appended claims.

I claim as my invention:

1. The process of treating nickel-iron base alloys in which the nickel plus iron content constitutes the predominating alloying constituents comprising, immersing the nickel-iron base alloy in a cold dilute acid bath wherein the alloy is an electrode, and subjecting the nickel-iron base alloy in the cold acid bath to the action of a low voltage alternating current having a current density of from 5 to 20 amperes per square inch for a period of time of up to 30 minutes for removing oxide film and intergranular oxidation and to give a clean smooth surface on the alloy, the bath being maintained cold during the entire period of treatment.

2. The process of treating nickel-iron base alloys in which the nickel plus iron content constitutes the predominating alloying constituents comprising, immersing the nickel-iron base alloy in a 5 to 20% cold sulphuric bath containing an inhibitor wherein the alloy is an electrode, and subjecting the alloy electrode in the cold acid bath to a low voltage alternating current having a current density of from 5 to 15 amperes per square inch at a voltage of from 2 to 12 volts for a period of time of up to 30 minutes while maintaining the bath cold during the entire period of treatment to remove predetermined amounts of surface metal therefrom and give the alloy a clean smooth surface, the inhibitor retarding solution of the nickel-iron base alloy when it is subjected to the alternating current.

3. The process of treating nickel-iron base alloys in which the nickel plus iron content constitutes the predominating alloying constituents comprising, immersing the nickel-iron base alloy in a cold dilute acid bath containing an inhibitor wherein the alloy is an electrode, subjecting the alloy electrode in the cold acid bath to the action of a low voltage alternating current having a current density of from 5 to 15 amperes per square inch at a voltage of from 2 to 12 volts while maintaining the bath cold during the entire period of treatment to remove the intergranular oxidation and give the alloy a clean smooth surface, the inhibitor retarding solution of the nickel-iron base alloy when subjected to the alternating current, withdrawing the alloy from the cold acid bath, and immersing the alloy in a neutralizing solution to neutralize the acid adhering to the surface of the alloy.

PHILIP R. KALISCHER.