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MANUFACTURE OF ALLOY FOILS

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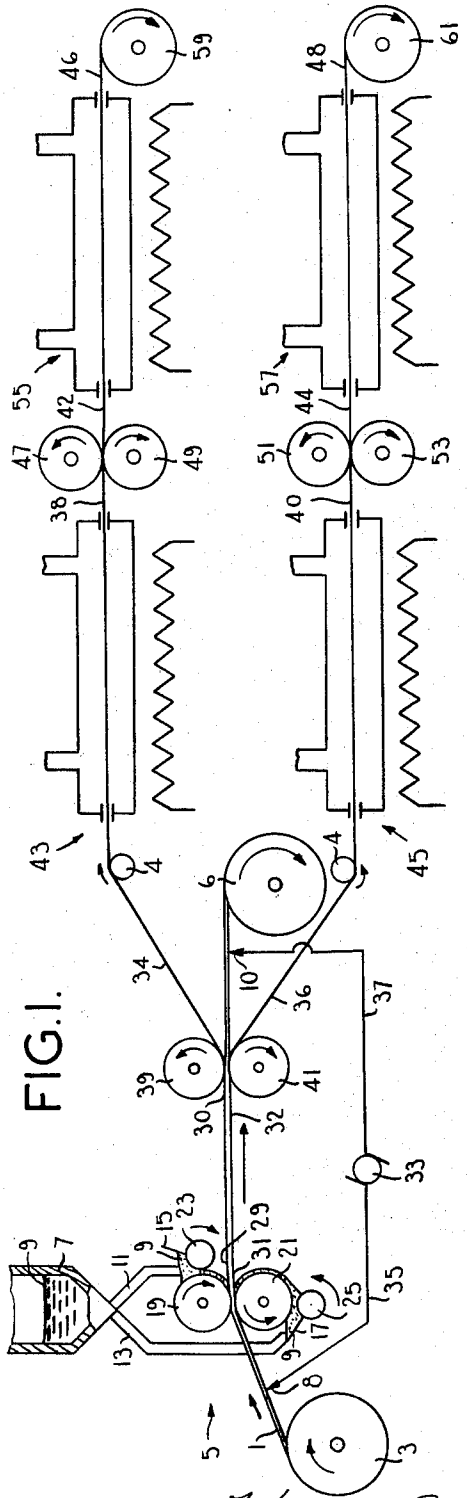


FIG. 1.

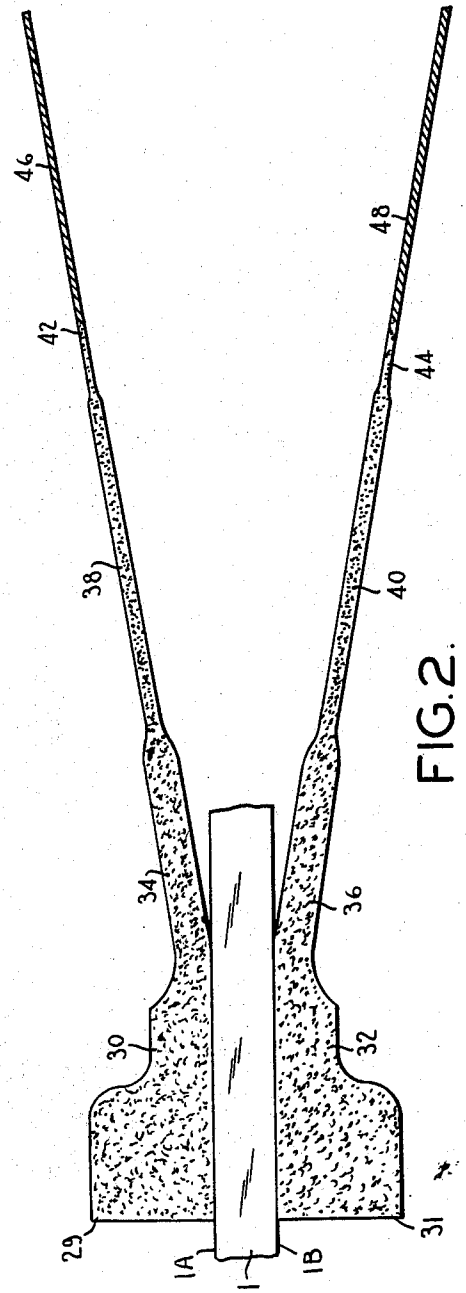


FIG. 2.

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MANUFACTURE OF ALLOY FOILS

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ABSTRACT OF THE DISCLOSURE

A flexible metal supporting strip is coated with a slurry composed of powders of different alloyable metals, a high-molecular-weight binder and a carrier liquid. The alloys to be formed are often brittle. The viscosity of the slurry is made such that when applied to the supporting strip it will evenly cling thereto in any posture of the strip. The strip is resistance-heated to dry the slurry thereon. Then the dried slurry is compressed sufficiently on the strip to green-bond the particles of the alloyable powders to one another but without embrittling alloying. The dried, green-bonded and compressed slurry, which at this time remains sufficiently flexible, is peeled from the strip. It is then sintered by heating a second time to a temperature high enough to drive off the binder and by diffusion and grain growth to improve the green bonds, but not high enough to effect embrittling alloying of the metal particles. Then the sintered strip is rolled for compaction to final gauge. The strip is then again sintered at a temperature high enough to homogenize by diffusion all of the constituent particles to form the desired alloy which may be brittle but no longer a problem since no more processing steps are required.

Among the several objects of the invention may be noted the provision of an improved apparatus and method for manufacturing improved thin sheets or foils of alloys from powders of the constituent metals, wherein uniformity of thickness and alloy composition is obtained throughout the foil; the provision of apparatus and a method for manufacturing foils of normally brittle metal alloys wherein the strip remains ductile during most of the manufacturing process, thereby simplifying working of the strip during such process; the provision of apparatus and a method for manufacturing a normally brittle alloy from elemental metal powders wherein formation of a homogeneous alloy of the metal elements (which causes brittleness) is delayed until other processing steps have been completed; and the provision of an improved dense and nonporous metal foil product. Other objects and features will be in part apparent and in part pointed out hereinafter.

The invention accordingly comprises the methods, apparatus and products hereinafter described, the scope of the invention being indicated in the following claims.

In the accompanying drawings, in which one of various possible embodiments of the invention is illustrated,

FIG. 1 is a diagrammatic view, parts being broken away, illustrating apparatus and steps for manufacturing metal strip or foil in accordance with the invention; and

FIG. 2 is a view illustrating diagrammatically modifications of certain materials which occur as they pass through the process.

Corresponding reference characters indicate corresponding parts throughout the several views of the drawings.

In the following description foil refers to thin sheet-metal alloy, the thickness being a few thousandths of an inch, usually about 0.001" to 0.008" or so. Powder means a finely divided substance. The average particle size is less than 50 microns with substantially no particles exceeding 100 microns in size. The exact size of the particles depends on the hardness of the metals involved, and the shape of the powder particles. The term slurry means a liquid medium of substantial viscosity containing metal particles suspended in a binder. The term binder means long-chain, high-molecular-weight organic compounds or the like characterized in that their constituents when comminuted are stringy and when mixed with a liquid such as water swell and act according to the invention to hold or bind the metal particles in suspension and to produce adequate viscosity in the slurry for adherence to a smooth surface. Thus the slurry will adhere evenly to metal surfaces contacted by it. Examples, but without limitation, of suitable binders are methyl cellulose, nonionic cellulose ether, polyethylene oxide, polyvinyl pyrrolidone et cetera. The intended use of the foil will determine the particular gauge to which it is manufactured. The drawings are illustrative and not to scale because of the small dimensions involved.

Briefly, the process for manufacturing foil according to the invention comprises coating a flexible preferably metal carrier strip with a slurry containing particles or powders of several different metals suspended in a binder, solidifying the slurry by heating to dry it, compacting and sintering it at a relatively low temperature to green-bond particles, and then compacting and sintering it a second time at a relatively high temperature to alloy the metals. The slurry includes a mixture of a long-chain high-molecular-weight organic compound acting as a binder, a carrier such as water, and powders of the constituent metals to make the desired alloy. When foil of an alloy is being manufactured, the powders of each of the various elemental metals of the alloy are supplied to the slurry in the proportion desired in the resulting alloy. The particles by mixing are evenly suspended by the binder. The amount of the binder used controls the viscosity of the slurry so that when applied to a metal surface it will cling thereto. For example, its viscosity may be from 1000 to 4000 cps. The percentage of solids therein may be 50% to 75%. The objects of this is that when evenly applied, the slurry will remain substantially even in any position of the metal surface. In some but not all cases a conventional wetting agent such as an aerosol may be used to advantage in the slurry.

Referring now to FIG. 1 of the drawings, a flexible metal carrier strip **1** is unwound from a reel **3** and fed to a roller coater generally designated **5** for receiving a coating of the slurry. Ultimately the carrier strip **1** is rewound on a reel **6**. The carrier strip is preferably composed of a hard metal, such as cold-rolled stainless steel, but if desired may be made of other appropriate material. It may be in the range of from .005" to .050" or so thick.

The roller coater **5** comprises a reservoir **7** which receives slurry **9** after it has been thoroughly mixed. The coater has two passages **11** and **13** through which the slurry is delivered to an upper trough **15** and a lower trough **17**, respectively. As carrier strip **1** moves through the coater **5** in the direction indicated by the arrows in FIG. 1, it passes between spaced upper and lower rollers **19** and **21** which are rotating in the direction indicated by the arrows. Roller **19** is at one side of trough **15** and is spaced from a metering roller **23** at the other side of the trough. The gap between rollers **19** and **23** determines the amount of slurry carried by the roller **19** to the top side of carrier **1**. Similarly, roller **21** is above trough **17** and the distance it is spaced from metering roller **25** beneath the trough determines the amount of slurry carried by roller **21** to the underside of the carrier **1**. With rollers **19**, **21**, **23** and **25** rotating in the directions indicated by the arrows, the upper and lower surfaces **1A**, **1B** (FIG. 2) of the carrier become uniformly coated with layers of slurry **9** from the troughs **15** and **17**. The wet

slurry coatings applied to carrier 1 are indicated at 29 and 31 in FIG. 2. By changing the spacing between the pairs of rollers at each trough, the amount of slurry metered to the carrier and thus the thickness of the coatings 29 and 31 may be varied. Preferably the coatings are substantially the same thickness but may be different. The coatings are held on the carrier at this time by the binder which adheres to the surfaces 1A and 1B (FIG. 2) of the carrier. Coating thickness may be .010", for example, when wet.

Next the coatings 29, 31 are dried on the carrier. The dried coatings are designated 30, 32. The means illustrated in the drawings for drying the wet coatings 29 and 31 comprise resistance heating of the strip 1 by connecting a source of electric current 33 to the strip 1 through conductors 35, 37, including brushes, as indicated at 8 and 10. The electrical resistance strip 1 results in heat being conducted to the wet coatings 29 and 31 which as they move forward reach the dry condition 30 and 32. While the thickness of coatings 29 and 31 may vary, a dried thickness at 30 and 32 of about 0.005" or 0.006" for each coating has been found satisfactory for producing a final foil thickness of about .0015" to 0.002".

Strip 1 with the dried coatings 30 and 32 thereon is then passed between rolls 39, 41 of a conventional roller mill. Rolls 39, 41 compact the coatings 30 and 32, thereby reducing their thickness and increasing their density in the aggregate, as indicated at 34 and 36. Preferably these rolls 39, 41 effect a reduction in the dry coating thickness in the range of from 10% to 50% or more. Thus a thickness of about .0025" to 0.003" may be obtained from an original thickness of about 0.006", which is satisfactory. The dry coatings 30 and 32 are compacted in the rolling mill an amount sufficient to effect sufficient green bonding in the solid phase between adjacent particles of metal in the coating, thereby providing a sufficiently cohesive metallic structure to be handled in the remainder of the process. However, the particles do not green-bond to the strip 1 because of the particle size, shape and hardness. It will be understood that bonding of the particles to the strip is inhibited by the following characteristics: softness of the particles in relation to the strip, certain particle shapes such as flat or acicular, and small particle size. It will be understood that the pressure required for the requisite reduction of the dried slurry is preferably not such as to reduce the thickness of the backing strip 1.

The coatings 30 and 32, when dried and compacted by reduction as at 34 and 36, are peeled from strip 1. The carrier strip 1 is then wound on reel 6 and, since the coating has not bonded to the carrier strip during compaction by the rolling mill, the carrier strip can be reused with little or no cleaning or other work being performed on it. Stripping of the compacted dried coatings 34 and 36 from the carrier strip 1 is facilitated by guide rollers 4 and a naturally occurring curling phenomena sometimes called "alligatoring." This is the tendency of two sheets being rolled to curl away from one another at the roll exit. Thus the dry coating 34 tends to curl up as viewed in FIG. 1 while the dry coating 36 tends to curl down, thus facilitating drawing away of the coatings from the carrier strip.

Next coating 34 is sintered in a furnace 43 and the coating layer 36 is sintered in a furnace designated 45, being guided by rollers 4. Furnaces 43 and 45 may be conventional heating furnaces for sintering and may be provided with inert protective or reducing atmospheres such as argon, hydrogen or the like, depending upon the nature of the metal constituting the starting powdered metal. Coatings 34 and 36 are sintered at a temperature which is sufficient to remove by vaporization most, if not all, dried binder in the coating, and by diffusion and grain growth effecting improvement of the solid-phase green bonds between metal particles of at least one of the metal powder elements in the coating. However, the sintering temperature is low enough to prevent any substantial homogenization or alloying between particles of different elements in the coatings. Any substantial diffusion of unlike particles of metal in the layers to homogenize and alloy such particles at this time is avoided, since it would cause embrittlement of the coatings 34 and 36 and make it difficult further to process. The coatings at this stage are designated 38 and 40 in FIG. 2.

Next the coating 38, which at this time is not brittle, is compacted to the desired final gauge of the strip or foil by passing the coating between two squeeze rolls 47 and 49 of a conventional rolling mill. In a similar manner the coating 40 is compacted to final gauge by a pair of squeeze rolls 51 and 53. The density of the coatings is somewhat increased as a result of this second compaction. Another purpose is smoothing and final sizing. In this case reduction may be 5% to 40% or so. The compacted coatings are designated 42 and 44. The coatings may be rolled at this time without difficulty since they are still ductile.

After the coatings 42 and 44 are rolled to final gauge, they are heated in furnaces 55 and 57 at a temperature higher than the temperature in the furnaces 43 and 45. The temperature in furnaces 55 and 57 is sufficient to homogenize all of the constituent particles to form the desired alloy. This occurs by substantially complete diffusion between all like and unlike particles of constituent metals in the coatings. The finished strips or foils of metal or metal alloys are designated 46, 48 and they may be rolled into coils as shown at 59 and 61. The resulting strips 46, 48 are very dense and substantially pore-free. The final alloying may cause embrittlement of the foil, but this is not detrimental since manufacture of the foil is complete.

The following is a particular example of how the process of the invention has been performed to make a brazing alloy which is brittle.

A slurry for a nickel-based brazing alloy was prepared containing by weight 4.5% silicon powder, 3.5% boron powder and 92% nickel powder. These ratios are equivalent to those in the known AMS 4778 brazing alloy. The elemental metal powders were mixed with a polyethylene oxide binder and water as a solvent. The nickel used was a carbonyl nickel (INCO type 255 or the equivalent) which, being fine i.e. 2 to 14 microns in average particle size, is easily sintered at low temperatures over a short period of time. This also favors later stripping away from carrier 1. The slurry was thoroughly mixed and placed in reservoir 7 of reverse roller coating apparatus 5. Thus a thin coating of the slurry (about .010") was applied to each surface of a hard, cold-rolled stainless steel carrier.

The coatings were dried on the carrier by resistance heating of the carrier (as shown at 30, 32). The dried thickness was about .005". The dried coating was then rolled down to about .0025" to compact the coatings (as illustrated at 34, 36 in FIG. 2 of the drawings). This effected initial green bonding between the particles themselves. Due to the small average size of the metal particles, there was no bonding between the metal particles and the carrier. Compaction of the coatings was accomplished without the rolls 39, 41 touching strip 1 and without reduction in its thickness.

The green-bonded compacted coatings were peeled off the carrier strip as they left the rolling mill and then passed through the first sintering furnaces such as shown at 43 and 45. The green-bonded compacts were sintered in furnaces 43, 45 at a temperature of about 1400° F. for about 30 seconds to one minute, which was sufficiently high to cause densification of the foil or coating layer and a substantial increase in the nickel-to-nickel bonds in the coatings. Some shrinking occurred to .002". This is illustrated in FIG. 2 of the drawings, where the portion of the coatings designated 38, 40 diagrammatically illustrates nickel particles bonded together as a matrix with the Si and B particles held therein. Sintering in the first

furnaces 43 and 45 removed a major part of the binder, leaving a dense layer. However, the temperature in furnaces 43 and 45 was beneath the temperature at which sufficient diffusion could take place between particles of the three powders to form any brittle alloy. Diffusion between these unlike particles at this time would cause embrittlement of the foil and make it difficult to effect final processing. The partially sintered strips were then rolled to finished gauge of about .0015" by the rolls 47, 49, 51 and 53. These rolls perform what is sometimes called a kiss pass, meaning that it smooths and finally sizes the product to foil dimensions. However, the kiss pass may reduce thickness as much as 40% or so. Finished foil thicknesses of from about 0.001" to 0.008" have been made successfully. Brazing foils are normally used at thicknesses in that range. Next the product was resintered in furnaces such as 55 and 57 for 30 seconds to one minute at a higher temperature of about 1600° F. to homogenize and alloy by diffusion of the three different metals in the coating and by grain growth to bring about alloying. The times consumed in the furnaces are variable, depending upon temperature and the metals that are being sintered. Thirty seconds to a minute is generally satisfactory.

Self-sintering of the type 255 INCO nickel powders referred to above occurs at approximately 1200° F. On the other hand, nickel-silicon-boron homogenization takes place rapidly above 1500° F. Therefore, by selecting said type 255 nickel powder (or the equivalent) I have been able to produce a strong metal foil by first sintering the coating or foil at about 1400° F. (in the furnaces designated 43 and 45) and then resintering the foil (after it is rolled to finished gauge) at about 1600–1700° F. to produce a homogeneous nickel-silicon-boron alloy which melts completely during brazing at about 1950° F. The finished foil is very dense and substantially pore-free.

By delaying homogenization of the unlike metal particles forming the alloy until after the alloy has been rolled to its finished thickness, brittleness does not occur until after final gauge is obtained. Thus the coating or strip being produced is easily worked to the desired gauge by conventional equipment, whereas subsequent to homogenization of the alloy the strip may be too brittle to process except by special equipment or processes. The strip or foil manufactured by my process is almost 100% metal, the binder and solvent having been vaporized and removed by heating during drying of the coatings and/or by heating in the sintering furnaces.

Another brazing alloy that may be made according to the invention is one constituted by nickel, silicon and chromium particles, the chromium being substituted for the boron in the above-described process. The weight ratio of nickel to silicon to chromium is 71:10:19. Temperatures used in the process in this case are like those above given, except that homogenization takes place at about 1700° F–1800° F., the temperature employed for brazing being about 2150° F.

Other examples of powders that may be used are iron and aluminum, with iron in the range of 80% to 90% by weight, and aluminum 10% to 20% by weight. In this case the sintering temperature is on the order of 900° F. or less, and the alloying temperature about 1,000° F. or more.

Another example of powders that may be used are copper and titanium powders in a 90% to 10% weight ratio, employing temperatures of 500° F. to 600° F. for sintering and about 1,000° F. or more for alloying.

Another example comprises the use of nickel and titanium. In this case the weight of nickel powder would be in the range of 70% to 75%, and the titanium 25% to 30%. In this case the sintering temperature is about 950° F. or less, and the allowing temperature about 1,000° F. or more.

The above-listed materials to form alloys are given by way of example and there are others unnecessary to mention because those useful according to the process will be clear from the above.

It may be mentioned that the use of the wetting agent in the slurry is not always required. Thus it is not required when polyethylene oxide, nonionic cellulose ether or polyvinyl pyrrolidone are used as the long-chain, high-molecular-weight organic compound to form the slurry. Also, while in the example the coatings 29 and 31 are applied to strip 1 by roller coating, they could be applied by passing the strip up through a tank, by brushing or by other suitable means for applying a uniform coating on the carrier strip.

It will be understood that although the principles of the invention have bene described in reference to three-component and two-component alloys, these principles would be applicable to an alloy consisting of any other number of components, provided the particulate forms of some of the components can be green-bonded and remain nonbrittle at a temperature lower than the temperature required for homogenizing all of them to form the desired alloy which may be brittle.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As various changes could be made in the above methods, apparatus and products without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The method of manufacturing an alloy foil, comprising:
applying a coating to a supporting carrier, said coating containing a binding compound and a combination of particles of at least two different metals,
drying the coating on the carrier,
squeezing the dried coating on the carrier to reduce the thickness of the coating and green-bond at least some of the particles,
removing from the carrier the coating containing the binding compound,
heating the removed coating at a comparatively low temperature to drive off most of the binding compound and to improve the green bonds between the particles in the coating without homogenization sufficient to form an alloy,
squeezing the removed coating to reduce its thickness,
and heating the removed coating at a comparatively higher temperature to homogenize all of the constituent particles to form the alloy foil.

2. The method of manufacturing an alloy foil, comprising:
coating a supporting carrier strip with a layer of a slurry containing a binding compound and a combination of particles of at least two different metals, the particles of one of which are in excess,
drying the layer on the strip,
squeezing the dried layer on the strip to reduce the thickness and green-bond at least some of the particles which are in excess,
removing the layer from the carrier,
heating the removed layer at a comparatively low first temperature to drive off binding compound and to improve the green bonds of the particles which are in excess without homogenization sufficient to form an alloy,
squeezing the removed layer to reduce its thickness,
and heating the removed layer at a comparatively higher second temperature to homogenize substantially all of the constituent particles to form an alloy.

3. The method according to claim 2, wherein groups of constituent particles contained in the binding compound and the first and second temperatures in order for the respective groups are as follows:

nickel, silicon and boron, with nickel in excess at first and second temperatures of about 1400° F. and about 1600° F. to 1700° F.;

nickel, silicon and chromium, with nickel in excess, at first and second temperatures of about 1400° F. and about 1700° F. to 1800° F.;

iron and aluminum, with iron in excess, at first and second temperatures of about 900° F. or less and about 1000° F. or more;

copper and titanium, with copper in excess, at first and second temperatures of about 500° F. to 600° F. and about 1000° F. or more;

nickel and titanium, with nickel in excess, at about 950° F. or less and about 1000° F. or more.

4. The method of manufacturing a metal alloy foil, comprising:

coating on each side of a metal carrier strip, a layer of a slurry containing a binding compound and powders of at least two elemental metals,

sending electrical current through the carrier strip to dry the layers on the carrier strip,

squeezing the dried layers on the carrier strip to reduce the thickness of the layer to effect green-bonding between most particles of the elemental metals in the layer,

removing the dried and squeezed layers from the carrier strip,

sintering the removed layers at a temperature sufficiently high to drive off binding compound and improve the green bonds between the particles of one elemental metal without effecting such diffusion between other metal particles as might cause alloying,

squeezing the sintered layers to substantially finished gauge,

and sintering the layers at a temperature sufficient to homogenize metal particles of the different elemental metals to form a metal alloy.

5. The method of manufacturing foil as set forth in claim 4, wherein initial squeezing of the dried layers is effected by rolling the layers while they are on the carrier strip by opposed rolls on opposite sides of the carrier strip, the rolling being at a pressure less than that which will reduce the thickness of the carrier strip or to force the metal particles into the carrier strip.

6. The method of manufacturing thin metal alloy foil, comprising:

making a slurry containing a binding compound and powdered metals, the powdered metals being the elemental metals of the desired alloy and being present in a ratio corresponding to the percent desired in the foil,

uniformly coating two opposite surfaces of a metal carrier strip with thin coatings of the slurry,

sending electrical current through the carrier strip to resistance-heat it thereby to heat the slurry coatings on the carrier strip to dry them,

roll-squeezing the dried coatings by opposed rolls on opposite sides of the coated carrier strip to reduce the thicknesses of the coatings and effect green-bonding between particles of elemental metals in the coatings,

removing both coatings from the carrier strip,

sintering the removed coatings at a temperature which is sufficiently high to cause densification of the dried coatings and increase the bonds between the particles of metal of the said one element without effecting any substantial alloying between particles of metals of different elements,

roll-squeezing the sintered coatings to reduce their thickness substantially to the desired finished gauge for the foil,

and sintering the rolled coatings at a temperature sufficient to homogenize metal particles of elements in each strip to form metal alloy foil strips.

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