

Dec. 24, 1940.

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2,225,868

COMPOUND METAL STOCK

Original Filed Nov. 7, 1933

2 Sheets-Sheet 1

Fig. 1.

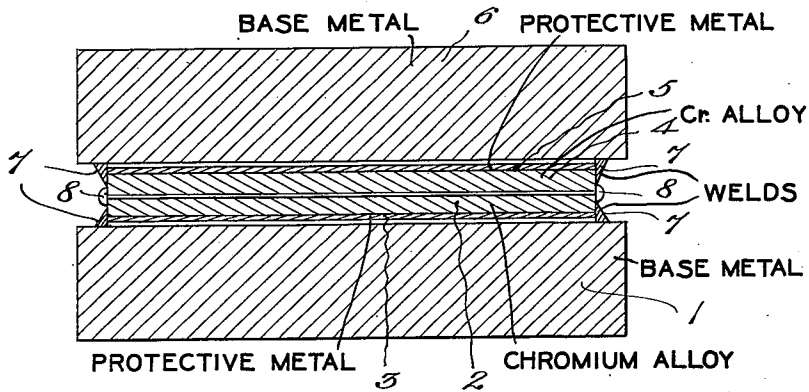
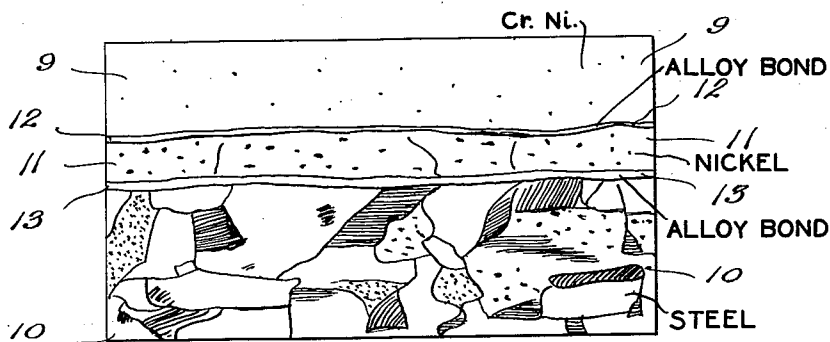


Fig. 2.



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2 Sheets-Sheet 2

Fig. 3.

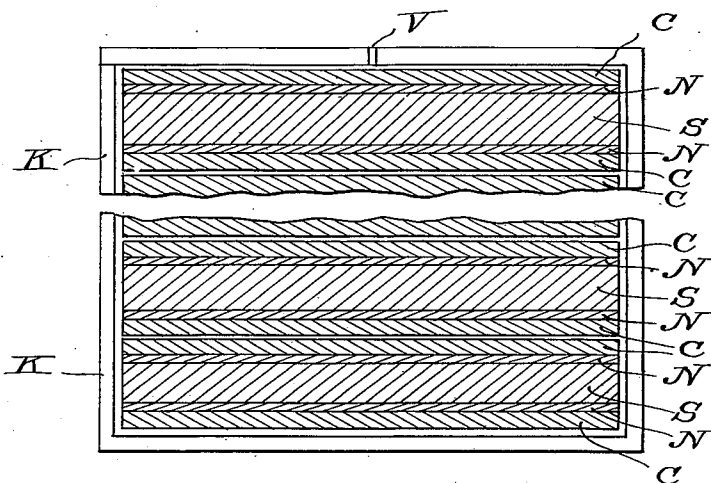
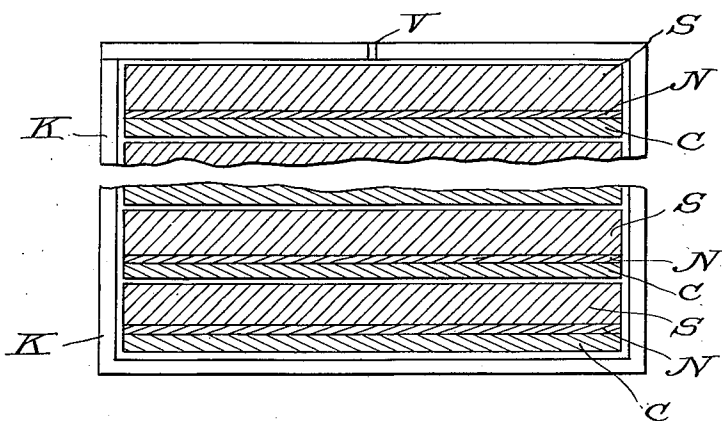


Fig. 4.



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COMPOUND METAL STOCK

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Original application November 7, 1933, Serial No. 696,946, now Patent No. 2,147,407, dated February 14, 1939. Divided and this application December 21, 1938, Serial No. 246,946

9 Claims. (Cl. 29—181)

The present invention relates to clad metal products containing chromium, and more particularly to composite metals integrally united and having a portion containing chromium.

Heretofore various methods have been proposed for the production of clad metal products, especially clad metal products in which the base metal or the cladding metal contains chromium. These prior methods involved certain disadvantages and produced product having shortcomings and/or defects. One of the worse disadvantages of prior clad products containing chromium was that the clad product could not be subjected to certain stresses and certain operations without the cladding metal tearing from the base metal. For instance, the bending and particularly the twisting of prior clad products containing chromium tore the cladding metal from the base metal. Although the art was struggling for a solution to the outstanding problem, none as far as we are aware, was wholly successful and produced a completely satisfactory product.

We have discovered a method of producing clad metal products containing chromium which is free from the disadvantages and shortcomings noted hereinabove and which is capable of producing satisfactory, successfully and commercially acceptable composite products.

It is an object of the invention to provide a clad metal product containing chromium which can be bent and twisted without failing and without coming apart.

It is also within the contemplation of the invention to provide a clad metal product containing chromium which consists of a backing or base metal which is relatively cheap or which has some desirable properties not possessed by the surface coating and a cladding metal or alloy which may be used to cover one or both surfaces of the base metal or alloy which contains chromium and which has superior corrosion and/or heat resisting properties.

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

Fig. 1 is a sectional view, somewhat diagrammatic of a pack of plates to be bonded by the present method;

Fig. 2 is a diagrammatic illustration, somewhat exaggerated, of a photomicrograph of a

section of the improved product showing the bond thereof;

Fig. 3 depicts a sectional view of a stack of plates encased in a metal container for double cladding; and

Fig. 4 depicts a sectional view of a stack of plates encased in a metal container for single cladding.

Generally speaking, the present discovery contemplates the provision of a film containing nickel or a nickel alloy to envelope or to coat the metal or alloy containing chromium. By incorporating the foregoing provision in the process of producing clad metal products, it is possible to produce such products on an industrial scale readily and uniformly. The complete explanation of how the nickel film functions in the production of a satisfactory and successful composite product containing chromium has not been definitely established. As a theory, we believe that the nickel or nickel alloy forms a bond having high physical properties by partial interdiffusion into not only the chromium containing metal or alloy but also into the base metal especially during the subsequent hot working operations, and that the nickel film protects the surface of the chromium-containing alloy when it is heated. It is to be noted that the foregoing is merely advanced as a theoretical explanation of the success of the present method, but it is to be understood that if such explanation is found to be incorrect, it is to be disregarded.

Broadly stated, the invention contemplates the production of a clad metal product containing chromium which comprises a base metal or alloy, a cladding or coating metal or alloy containing chromium and an intermediate layer or film containing nickel or a nickel alloy which is adhesively united to the entire face of said chromium-containing cladding metal to form an integral unit. In carrying the invention into practice, the surface of the chromium containing metal or alloy is adhesively coated with a film of nickel or a nickel containing alloy and the base metal having a clean surface is contacted firmly against the film of nickel and the two base metal and cladding metal are secured together in some appropriate manner as by clamping, weighting, welding, or the like. The composite product is then heated to a relatively high temperature preferably in a reducing atmosphere. If a stack of layers are piled on each other, the weight thereof may be sufficient to cause the base metal to stick to or bond with

the film of nickel on the chromium-containing cladding plate or sheet. In some cases, a heavy weight on the stack may be used to effect the sticking or bonding of the sheets. In the event that a composite product like the one shown in Fig. 1 is being made, hot working such as rolling, forging or the like may be employed. The heated composite product is then subjected to working operations such as forging, rolling or the like. After the bonding of the various layers has been accomplished not only hot working but also cold working may be employed. In the finished product the base metal or alloy and the cladding or coating metal or alloy are integrally united so thoroughly and effectively that the product can be stressed and deformed severely without rupturing the bond between the base and the coating. It is to be noted that the new composite product is particularly valuable where the product is to be used in structures which are subjected to severe stresses or where the product is to be subjected to severe fabricating operations. For instance, the improved product even in its reduced or worked condition can be twisted into a helix or the like without the cladding metal tearing away from the base metal.

For the purpose of giving those skilled in the art a better understanding of the invention the following specific example is given for the purpose of illustration.

A plate which is composed of chromium-nickel alloy and which is $\frac{3}{8}$ of an inch thick and of any desired length and width is cleaned in any appropriate manner, such as by sand blasting, pickling or the like. In this manner, a clean and scale-free surface is produced. To this cleaned surface a film of nickel or of a nickel alloy is applied. The application of the nickel film may be effected, for instance, by electroplating or by metal spraying or by any other suitable process.

In practice, it is preferred to apply the film of nickel or nickel alloy by means of electrodeposition. In the event that only one surface of a plate is to be clad, it is preferred to place two equal sized plates back to back and secure them together by means of suitable clamps or the like. The clamped plates which may be constituted of a chromium containing metal or alloy such as a chromium nickel alloy, is immersed in an electrolyte having a suitable composition for the electrodeposition of nickel or of a nickel alloy.

A film, coating or layer of nickel or nickel alloy is electrodeposited upon the cleaned surfaces of the plates arranged back to back. The electrodeposition is conducted in any appropriate manner to yield a dense, adherent deposit of nickel or nickel alloy. For instance, the chromium containing plates may be cleaned in the usual manner by treating them as cathodes in an electrolytic alkaline cleaning bath. After this operation the plates are rinsed in hot water and are immersed in a solution of muriatic acid containing 5% by weight of hydrochloric acid and heated to a temperature of about 150° F. They are held in the acid solution for several minutes which removes oxide or other surface films of a type tending to interfere with welding by heat and pressure and are then transferred directly to a nickel plating bath where the coating of nickel is electrodeposited. The nickel coating is thus deposited on a cleaned surface of the chromium containing plate and protects said surface against reformation of oxide or other surface films that would interfere with welding

during subsequent heating and working operations. It is preferred to apply a coating of nickel having a thickness of about 0.002" to about 0.005". Of course, the thickness of the film or coating of nickel may vary considerably. Satisfactory results have been obtained from nickel coats having a thickness as low as 0.001 of an inch and as thick as 0.005 of an inch. Of course, films having thicknesses more than about 0.005" or less than 0.001" may be used.

In conducting the electrodeposition of nickel any suitable nickel plating solution may be used. It is preferred to use the following nickel plating solution and the following operating conditions:

Temperature.....	130 to 150° F.
Agitation.....	Moderate air agitation
Current density.....	50 amp. per sq. ft.
Nickel sulphate.....	44 oz. per gallon
Nickel chloride.....	2.2 oz. per gallon
Boric acid.....	4.0 oz. per gallon
Sodium sulphate (anhydrous).....	13.8 oz. per gallon

The nickel coated plates containing chromium are assembled in one composite pack or billet which may have any suitable arrangement. A satisfactory assembly of the pack is diagrammatically illustrated in Fig. 1 of the drawings.

Steel slabs 1 and 6 which have a thickness of about $\frac{3}{8}$ " and of slightly greater width and length than the nickel plated chromium containing plates have at least one surface cleaned in an appropriate manner such as machining, sand blasting, grinding or the like. In this manner, a dry, grease-free, clean steel surface is obtained.

In setting up the stack or pack, it is preferred to lay steel slab 1 flat upon the floor with its clean surface facing upwardly. Upon steel slab 1 is placed the chromium containing plate 2 with the nickel coated surface 3 in contact with the clean surface of steel slab 1. A second chromium containing plate 4 is laid upon the first chromium containing plate 2 with its nickel coated surface 5 exposed upwardly. Upon the nickel coated surface, a second steel slab 6 is placed with the clean surface in contact with the nickel coated surface 5. In practice, it is preferred to use welds 7 to secure the steel plates to the chromium-containing plates and to use welds 8 to secure the chromium-containing plates together, as may be clearly seen in Fig. 1. It is to be noted, however, that these welds should preferably be discontinuous and should be disrupted at one or more points to provide vents in order to permit the escape of the expanding gases.

In the foregoing manner, a composite pack or billet is formed in which the clean surface of the steel slab and the nickel coated surface of the chromium containing plate are held together. The composite pack is heated to a temperature suitable for bonding. In the present instance where a steel slab is being clad with a plate of an alloy of chromium and nickel, a temperature of about 2000° F. to about 2300° F. is preferred. The heating is effected preferably in a reducing atmosphere. When the entire pack has reached this temperature it is hot worked in an appropriate manner, as for example, hot rolled. It has been found that only a small amount of hot working is necessary to secure a good bond between the steel slab and the nickel coated plate containing chromium. In other instances, however, it has been found that a great reduction

in area can be effected, if desired. By hot rolling the aforesaid pack, it can be reduced to an appropriate over-all thickness. In the present instance, it was reduced to about $\frac{1}{2}$ of an inch.

After the pack has been worked or rolled to the desired extent the edges thereof can be trimmed. In this manner, two clad steel products are produced each of which are about $\frac{1}{4}$ of an inch in thickness. The cladding is equal to about 10% of the total thickness. Of course, the amount of cladding can be varied depending upon the particular conditions. For most practical purposes, the thickness of the clad metal is from five to twenty per cent of the total thickness, depending on the thickness of clad metal needed to withstand the particular conditions of corrosion, abrasion, scaling, etc.

In Fig. 2 a diagrammatic illustration of a photomicrograph of the product produced in accordance with the foregoing method is depicted. It will be observed that the reference character 9 depicts a portion of the alloy of chromium nickel and reference character 10 depicts a portion of the steel layer. Between the two layers 9 and 10 is an intermediate layer 11 constituting the nickel coat. Between the nickel layer and the steel layer is a bond 13. In the same way, between layer 9 and 11 is a bond 12 constituting an oxide-free diffusion zone of the metal of the layer 9 in the protective layer 11. It was found that the product produced in accordance with the present method could be subjected to severe stresses and could be subjected to various fabricating operations. Not only could the product be subjected to stresses and fabricating operations, but it could also be subjected to intense bending and twisting without the cladding metal tearing from the base plate of steel or without the bonds rupturing or failing in any way. As a result of practical tests it has been found that the present product can be produced on an industrial scale and the product used commercially.

Under certain conditions, it may be desired to heat a multiplicity of composite products at one time. For instance, if it is necessary to obtain a large production from a furnace in a short period of time, then it is preferred to use the arrangement shown in Fig. 3. In this figure, the reference character K designates a metal container which completely encloses the composite products to be bonded. In practice, it is preferable to employ sheet metal, such as sheet steel, for container K because of its light weight, its ability to expand freely, its low cost, its adaptability for folding, welding, etc. and its easy cutting properties. Of course, the conventional containers or boxes of cast metal or alloy may be used, if desired.

It is to be observed that chromium containing plates 2 and 4 do not weld to each other because their contacting surfaces have not been nickel coated. Moreover, it is preferred to leave the surfaces of plates 2 and 4 which are to be plated back to back in an uncleaned condition. Furthermore, the surfaces placed back to back can be coated with some refractory material or the like which will eliminate all possibility of plates 2 and 4 being stuck together mechanically or otherwise.

It is to be noted that the present invention provides useful products. Thus, a composite metal may be produced which is cheaper than a solid alloy of the same composition as the cladding metal or alloy while at the same time possessing the desirable corrosion and/or heat resistance of

the chromium containing cladding, and that the composite metal possesses overall properties superior to either the solid base metal or alloy, or the solid coating or cladding metal or alloy. For example, stainless steel clad copper would have the corrosion resistant of stainless steel but would have a considerably greater heat conductivity than stainless steel.

A stack of plates may be arranged as shown in Fig. 3 with a chromium-containing plate C at the bottom. This plate is placed so that the nickel film N faces upwardly. Upon the nickel film, a steel plate S is mounted. A second chromium-containing plate C with a nickel film N facing downwardly engages the top of steel plate S. This stack of plates is herein termed a "set."

As many sets as desired may be stacked up. A sheet of steel may then be folded around the stack and secured together as by welding or the like. In order to completely enclose the stack, end portions of sheet steel may be welded to the open ends of the folded sheet. For the purpose of permitting the escape of gas from the welded container, a vent V may be provided, preferably in the top of the container.

That stack of sets enclosed in the container is heated sufficiently high to effect bonding of the nickel to the adjacent faces of the steel plates. Due to the fact that the stack is sealed in a container, the heating is practically independent of the furnace atmosphere. If the weight of the stack is heavy enough, the nickel will be stuck or united to the steel. Usually, it has been found sufficient to press down on the top of the stack. For instance, a heavy plate, weight or the like may be placed on the top of the stack or the stack may be placed in a hydraulic press. After this each unit set may be subjected to working operations, such as hot or cold rolling, forging, etc. When the units have been worked or reduced to the desired extent, the clad product is ready for fabricating operations to convert the same into articles of manufacture.

In the foregoing operations, it has been found that the bottom and top plates of chromium-containing material do not stick or bond to the adjacent walls of the enclosing container or stick together. It appears that a greenish scale is formed on the chromium-containing plates which prevents sticking or bonding. The composite units comprising a steel base plate having a nickel coated cladding plate containing chromium on each face of the steel plate may be taken from the stack and handled or treated separately. Under the influence of the conditions within the container including heat, pressure and atmosphere, a diffusion bond is effected between the nickel and the chromium-containing plate. In this manner the two chromium plates and intermediate steel plate are united into an integral double clad unit, of course, the integral double-clad units may be removed from the container by opening the same in any appropriate manner. If a container made of sheet steel is used, it can be easily cut apart and the stack of sets may be easily removed therefrom.

In the event that it is desired to single clad a metal or alloy, such as a steel plate, sheets or the like, an arrangement such as illustrated in Fig. 4 may be employed.

Within container K and at the bottom thereof, a chromium-containing plate C is placed with the surface bearing chromium in contact with the surface of the container which may be steel. The surface of the nickel film or layer N of the chro-

mium containing plate faces upwardly. Upon the nickel film or layer N, a steel plate S is mounted. Of course, the surface of the steel plate S, which makes contact with the nickel, is thoroughly cleaned as explained hereinbefore. A chromium-containing plate and a steel plate with a nickel film intermediate thereof is herein termed a single clad unit.

By placing a plurality of single clad units in container K, the latter may be filled and may then be closed as by welding or the like. A vent V is preferably provided to permit the escape of gases from the container K during heating operations.

In the event that it is desired, it is preferred to insert a separator between the top of the steel plate of any unit and the bottom of the chromium-containing plate of the next higher unit which makes contact with the steel plate. It has been found that one or more uncleaned sheets of chromium-containing material function satisfactorily as a separator. Of course, a layer of refractory material may likewise be used as a separator instead of the uncleaned sheets.

When the container is charged with single-clad units and is sealed, it may be introduced into a furnace and heated to a temperature of at least about 1800 to 2000° F. and preferably 2300° F. for a period of at least about 1/2 to 2 hours. In other words, the container is subjected to heat and pressure sufficient to insure the bonding of the steel plate to the nickel film or layer and of the latter to the chromium-containing plate to form an integral unit. The container may then be opened and each unit may be subjected to working, as rolling, forging and the like. By applying the desired amount of working, an appropriate reduction of area may be effected and the unit may be reduced to the desired size. The final product is a single clad unit which has such a tenacious bond that a sample of about 5 inches long may be subjected to a twisting test which involved twisting the sample through 360 degrees and then retwisting the sample to its original condition without the bond rupturing.

It is to be further noted that in the present instances the chromium nickel alloy contains 14% of chromium, 6% of iron and 80% of nickel but other chromium-containing alloys may be substituted therefor. Thus, for instance, any of the stainless steels, particularly those containing about 18% of chromium and about 8% of nickel may be used and steel clad products made with a clad of stainless steel may be produced. Similarly, copper or other metals or alloys containing little or no chromium can be substituted for steel to produce a composite product having a base of copper or the like and a cladding of a chromium-containing alloy.

It is also to be observed that the composite product can be subjected to the same fabricating operations as would be employed on a sheet or plate composed of the base metal. The composite product with steel as the base metal can be worked either hot or cold by spinning, pressing, drawing, flanging, bending, dishing, hammering, etc., and by the usual cold working operations such as shearing, punching and drilling; joining by riveting, welding, lock-seaming, soldering, etc. It is preferred to cold work the composite product clad on copper as a base, and it may be subjected to spinning, stamping, drawing, pressing, flanging, joining, etc.

Furthermore, it is to be noted that the addition of the bonded layer of chromium contain-

ing alloy to mild steel, copper, etc. gives added strength to the base metal and enables the composite product to be more highly stressed in tension, compression, or shear than would be safe with a plate or sheet of the solid base metal.

Moreover, the articles of manufacture which can be produced from the composite product include autoclaves, kettles, dye vats, soap boiling equipment, dairy tanks, truck tanks, beer fermenting and storage tanks, cooking utensils, and other equipment for the chemical, dairy, food products, and allied fields, and the home.

It is to be noted that the present invention is not to be confused with proposed processes in which a separate sheet of iron is laid between a steel plate and a chrome alloy plate. In this proposed process, it is necessary to provide special means in order to produce a bond for union between the various parts. Thus, a deoxidizing agent such as an aluminum powder or the like must be provided in order to dissipate oxygen gases which are present in the air spaces between the steel plate and the intermediate iron sheet and between the chrome alloy plate and the iron sheet. Furthermore, various fluxes have been proposed to facilitate the bonding of the various sheets and plates or the like. The present invention avoids the foregoing complicated process and provides a procedure which produces reliably, consistently and uniformly coated products with a tenacious bond throughout the interface of the connecting surface of the plates or the like which are to be joined together.

Although the invention has been described in conjunction with preferred embodiments, it is to be observed that modifications and variations may be resorted to as one skilled in the art can readily understand. Thus, various modifications can be made in the individual steps of the novel process and the invention can be applied to the production of coated wire, tubes, rods and the like by altering the shapes of the parts constituting the composite pack or billet.

Of course, equivalents of nickel or nickel alloys such as cobalt, iron and the like, may be employed provided the metal or alloy is adhesively united to the entire surface of the chromium-containing plate or the like in order to form an impervious protective film. For adhesively uniting the nickel or nickel alloy or equivalent metal or alloy to the face of the chromium-containing plate, electroplating, spraying by the Schoop process, or the like may be utilized.

The present application is a division of our co-pending application Serial No. 696,946, filed on November 7th, 1933, which has now matured into Patent No. 2,147,407, dated February 14, 1939, and having the title "Method of producing composite metals".

We claim:

1. A composite metal mass comprising a portion consisting of a ferrous alloy containing sufficient chromium to interfere substantially with welding by heat and pressure, an oxide-free diffusion zone adjacent thereto comprising a solid solution of metal of such chromium containing alloy in electrolytic nickel deposited in situ and additional metal merging into such electrolytic nickel and united thereto by welding.

2. A composite metal mass comprising a facing of corrosion-resistant metal, electrolytic nickel deposited thereon and diffused therewith substantially without intervening oxide and a backing of ferrous metal welded thereto.

3. A clad metallic product which comprises

a base metal, a clad of alloy comprised largely of metal selected from the group consisting of iron and nickel containing sufficient chromium to form a surface film tending to interfere with welding by heat and pressure, and a film of protective metal intermediate and interposed between said base metal and said alloy and being electro-deposited on said alloy, said protective metal being integrally bonded to said base metal and to said alloy substantially without interfering film to form an integral unit.

4. A clad metallic product which comprises a base of copper, a clad of alloy comprised largely of metal selected from the group consisting of iron and nickel containing sufficient chromium to form a surface film tending to interfere with welding by heat and pressure, and a film of nickel intermediate between said copper and said alloy and being electrodeposited on said alloy, said nickel being bonded to said copper and to said alloy substantially without interfering film to form an integral unit.

5. A clad metallic product which comprises a base of ferrous material, a clad of nickel alloy containing sufficient chromium to interfere with welding by heat and pressure, and a film of nickel intermediate and interposed between said ferrous material and said alloy and being electrodeposited on said alloy, said nickel being bonded to said ferrous material and to said alloy substantially with the interfering film to form an integral unit.

6. A clad metallic product which comprises a base metal, a clad of chromium-containing alloy having a face bonded to said base metal and comprised largely of metal selected from the group consisting of iron and nickel containing sufficient chromium to form a surface film tending to interfere with welding by heat and pressure, and a film of protective metal intermediate and interposed between said base metal and said alloy and being integrally incorporated as particles on said alloy to cover entirely the aforesaid face thereof, said protective metal being integrally bonded to said base metal and to said alloy substantially without interfering film to form an integral unit capable of being subjected to bending and twisting tests without the clad of chromium-containing alloy separating from the base.

7. A clad metallic product which comprises a base of copper, a clad of chromium-containing alloy having a face bonded to said base metal and comprised largely of metal selected from the group consisting of iron and nickel containing sufficient chromium to form a surface film tending to interfere with welding by heat and pressure, and a film of nickel intermediate between said copper and said alloy and being integrally incorporated as particles on said alloy to cover entirely the aforesaid face thereof, said nickel being bonded to said copper and to said alloy substantially without interfering film to form an integral unit capable of being subjected to bending and twisting tests without the clad of chromium-containing alloy separating from the base.

8. A clad metallic product which comprises a base of ferrous material, a clad of chromium-nickel alloy having a face bonded to said base and containing sufficient chromium to interfere with welding by heat and pressure, and a film of nickel intermediate and interposed between said ferrous material and said alloy and being integrally incorporated as particles on said alloy to cover entirely the aforesaid face thereof, said nickel being bonded to said ferrous material and to said alloy substantially without interfering film to form an integral unit capable of being subjected to bending and twisting tests without the clad of chromium-nickel alloy separating from the base.

9. A clad metallic product which comprises a base metal, a clad of chromium-containing alloy having a face bonded to said base metal and containing sufficient chromium to form a surface film tending to interfere with welding by heat and pressure, and a film of protective metal intermediate and interposed between said base metal and said chromium alloy and being integrally incorporated as particles on said alloy to cover entirely the aforesaid face thereof, said protective metal being integrally bonded to said base metal and said chromium alloy substantially without interfering film to form an integral unit capable of being subjected to bending and twisting tests without the clad of chromium-containing alloy separating from the base.

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