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METHODS FOR PRODUCING TITANIUM-CLAD METAL

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Fig. 1.

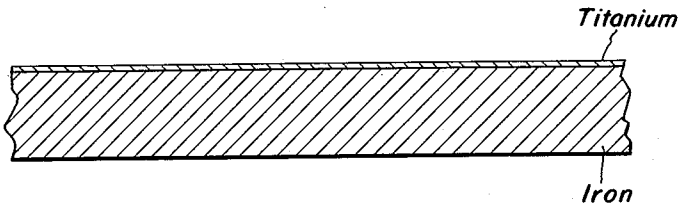
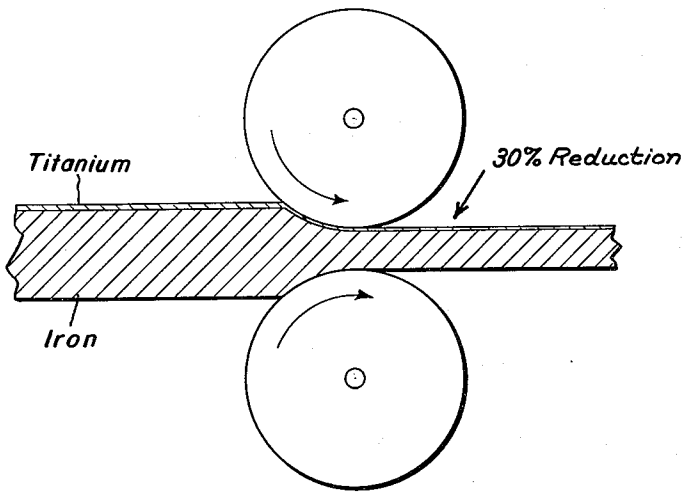


Fig. 2.



Inventor:
Floyd C. Kelley,

by Paul A. Frank
His Attorney.

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METHODS FOR PRODUCING TITANIUM-CLAD METAL

Floyd C. Kelley, Schenectady, N.Y., assignor to General Electric Company, a corporation of New York

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This invention relates to the provision of an adherent, corrosion-resistant coating of titanium on a different metal base. More particularly, it is concerned with the provision of an adherent, corrosion-resistant coating of titanium on a different metal base by cold-rolling and the fabrication of formed structural elements of titanium from such a composite material. This application is a continuation-in-part application of application Serial No. 432,329, F. C. Kelley, now abandoned, assigned to the same assignee as the present application.

The chemical and physical characteristics of substantially pure titanium suggest many advantages over other structural materials now in use. Unfortunately, some of the properties which render titanium desirable for certain applications have in the past prevented its use. For example, no economical way has been previously known to consistently provide a readily corrodible material, for example, iron, aluminum alloys, and the like with an adherent, corrosion-resistant, continuous coating of titanium. Further, because of certain of the mechanical properties of titanium, it has been previously deemed impractical to fabricate complexly shaped structural elements of relatively thin-walled titanium. My invention is concerned with methods of providing a titanium-clad base metal.

A principal object of this invention is to provide a method of cladding a metal with titanium.

A further object of this invention is to provide cold-rolled iron sheet having an adherent, substantially continuous coating of titanium on its surface.

Another object of this invention is to provide an aluminum body having an adherent, substantially continuous coating of titanium on a surface thereof.

Another object of this invention is to provide an aluminum alloy body having an adherent, substantially continuous coating of titanium on a surface thereof.

It is still a further object of this invention to provide a method of manufacturing formed structural elements of substantially pure titanium, and such elements made by said process.

Other objects and advantages of this invention will be in part obvious and in part explained by reference to the accompanying specification and drawings in which:

FIG. 1 is a section through a titanium-clad iron body made according to the present invention; and

FIG. 2 is a view showing a method for reducing the thickness of the titanium-clad iron body to effect bonding between the two metals.

FIGS. 1 and 2 are also illustrative of other titanium-clad bodies in accordance with the teachings of this invention, including for example, aluminum and its alloys.

Briefly stated, I have provided a method of cladding a base metal with an adherent, continuous thin layer of substantially pure titanium by cold rolling, a product produced by said process which has utility per se or as an intermediate which may be further fabricated and treated to produce formed, thin-walled structural elements composed of substantially pure titanium. In practicing my invention and the various aspects thereof, minor variations in procedure and adaptations of the end products may occur to those skilled in the art; consequently, I do not intend the several examples set forth in the specification to be construed as limitative but merely exemplary.

Titanium metal is produced at present by two processes, the so-called iodide process and the Kroll process. In the former, titanium iodide vapor is decomposed on a heated titanium wire, depositing pure titanium on the wire. In the Kroll method, titanium chloride is treated with metallic magnesium to produce metallic titanium sponge and magnesium chloride. The sponge is then melted and cast into ingots. Because of the difficulty of removing all the magnesium chloride from Kroll process titanium and due to the usual presence of somewhat larger amounts of oxygen and nitrogen, it is slightly less pure than titanium produced by the iodide process. ASTM specification places the following limits on high purity titanium with reference to the iodide process.

		Percent
Titanium	minimum	99.9
Carbon	maximum	0.03
Silicon	do	0.02
Iron	do	0.02
Aluminum	do	0.03
Nitrogen	do	0.01
Manganese	do	0.04
Others	do	0.01

A recent process called "The Electrolytic Process" also results in a pure form of titanium which may be employed in this invention.

One of the most important properties of titanium from a commercial and engineering standpoint is its resistance to corrosion. While titanium is highly reactive at elevated temperatures and will react readily with gases such as oxygen, nitrogen and hydrogen at temperatures above 600° F., at room temperature, it is practically inert with respect to these gases, oxidizing acids such at nitric and aqua regia, dilute sulfuric and hydrochloric acids and to most organic acids. It is resistant to dilute alkalies, as well. One of titanium's most spectacular properties is its resistance to corrosion by solutions of chloride. It is practically inert to sea water, to boiling dilute solutions of many chlorides and is unaffected by boiling saturated solutions of sodium chloride.

As previously pointed out, titanium has a very high affinity for certain of the gases present in the atmosphere at elevated temperatures. For this reason, it is very useful as a "getter" in vacuum apparatus. It functions to remove residual molecules of atmospheric gases in evacuated containers or systems in a manner well known to that art.

The singularly good resistance of titanium to corrosion by sea water has, of course, led to many attempts to clad steel and iron with titanium for marine and other uses where such an environment is encountered. Hot rolling techniques have been attempted but because of the extreme activity of titanium at temperatures necessary for hot rolling, it has been necessary to resort to pack rolling. In this, a titanium slab is placed in juxtaposition to an iron slab to be coated and the slabs enclosed in a gas-tight metal envelope which is then either evacuated or flushed with a noble gas. The pack is then heated, generally in a noble gas atmosphere furnace and hot rolled. In addition to the inherent difficulties and expense of such a procedure, this type of cladding has not produced consistently good bonding between the iron slab and the titanium.

Electrodeposition of titanium on iron has also been investigated. This method has several limitations in that the condition of the surface to be plated is critical, high bath temperatures are necessary and the high current densities required make the process of doubtful practical value.

I have discovered that under particular conditions, an

adherent, continuous coating of titanium may be applied to iron by a simple cold-rolling procedure.

A first example of my invention deals with the production of titanium-clad, cold-rolled iron upon which the titanium coating was applied to one side only.

A strip of cold-rolled iron 0.125 inch thick was annealed at about 1650° F. in hydrogen. After annealing, one face of the sheet was grit blasted and wire brushed. A similar size strip of titanium 0.004 inch thick was produced by arc melting iodide titanium in vacuum and cold rolling. After cold rolling, one of its faces was wire brushed. The two sheets were placed with their cleaned faces together and the two sheets secured together. One method I have found suitable is to "tack" or spot weld the sheets together at one edge (the entering edge to the rolls) in a few places, forming a composite sheet or work piece about 0.129 inch thick. This composite sheet was then cold reduced by a rolling mill having cast iron working rolls. In order to prevent the titanium from welding to the chilled cast iron working rolls under rolling stresses, a protective coating was applied to the outer surface of the titanium layer. Alternatively, of course, such a protective coating could be applied to the surface of the working roll. While many materials might be used for this protective coating, I have found commercial milk of magnesia, a suspension of magnesium hydroxide, $Mg(OH)_2$, in water, satisfactory for this purpose. A preferred method is to paint a thin layer of milk of magnesia on the titanium surface to be worked and permit the layer to dry, forming a substantially continuous coating. The composite titanium-iron strip or sheet was then cold reduced in one pass from about 0.129 inch to about 0.070 inch, a reduction of about 46 percent. The titanium was found to be securely welded to the iron after this initial pass. The composite sheet was then given a second heavy reduction in a single pass, reducing it to about 0.043 inch, or about 39 percent reduction. The composite sheet was then cold rolled in several passes to 0.005 inch sheet, amounting to a total cold reduction of 96 percent.

Upon careful examination, the titanium coating was found to be adherent, continuous and about 0.00015 inch thick. There was no indication of cracking, either along the edges or at any other portion of the surface, except for minor defects in the zones of the spot welds. These, however, were limited to the extreme edge and were removable by the normal trimming or slitting operation following rolling.

I have discovered that vacuum-annealed iodide titanium cold-rolled to 0.004 inch thick strip may be used in the foregoing example in place of the arc-melted titanium without adversely affecting the quality of the finished material.

I further subsequently discovered that when steel working rolls are used in place of chilled cast iron, the titanium does not tend to weld to the roll surface, rendering coating unnecessary.

Using a similar procedure, I have discovered that iron strip may be successfully clad on both sides simultaneously, by the expedient of starting with a composite strip of titanium-iron-titanium. In this case, of course, the protective coating must be applied to the titanium comprising both faces if cast-iron rolls are used.

In both of the above-cited examples, annealing was found unnecessary at any stage of the rolling. If for any reason annealing should be deemed necessary, it should be done in either a vacuum or an atmosphere inert to titanium at elevated temperatures.

As further demonstration of the tenacity and continuity of the titanium coating produced in this manner, cups about 0.125 inch in diameter and about 0.150 inch deep were cold drawn from the 0.005 inch titanium-coated iron. Even after this deep-drawing treatment, no separation of the layers could be detected, nor was any cracking observed. The iron was then dissolved, leaving a complete, integral, self-sustaining cup of cold-worked titanium having no observable holes or other structural defects. The iron may be removed in any suitable manner, for example, by means of dilute hydrochloric acid. The wall thickness of the titanium elements thus obtained was of the order of 0.00015 inch or less. Obviously the thickness may be varied depending upon the initial dimensions of the work piece and by the amount of working. The form of the resulting titanium element is not restricted to cup-form, nor to deep drawing operations. It is, therefore, apparent that structural elements of substantially pure titanium may be conveniently made by forming the desired shape from the clad composite material by drawing, bending, machining or any suitable process and then dissolving the base material from the titanium. In this manner, complexly shaped strong structural elements of very thin titanium metal may be economically mass produced. Elements of this type are suitable for use as load bearing elements in evacuated apparatus. Complexly shaped electrodes, heating elements or the like, may advantageously be made from thin-walled titanium in this manner. By providing means for heating these elements, efficient "gettering" may be provided over long periods of time, and any tendency for the evacuated apparatus to become "gassy" may be effectively countered.

I have further discovered that the successful practice of this process requires substantially pure titanium. When iodide titanium was used consistently good results were obtained. On the other hand, when Kroll process titanium was used, the titanium did not consistently weld to the iron satisfactorily during the first heavy pass, and during subsequent reduction, the titanium adhered to the iron only in a few places and separated in others to form a lace-like, non-continuous texture which exposed the iron base through its openings. Kroll process titanium is known to be somewhat less ductile than iodide titanium. Presumably in this case, the iron deformed more readily than the titanium and pulled the relatively thin titanium layer apart in zones of non-adherence.

Additionally, I have discovered that because titanium tends to work harden and thus lose ductility, it is important that the first pass through the working rolls accomplishes a large reduction. Indifferent or poor adherence and continuity result unless a heavy first draft of at least 30% or more is taken. Therefore, I regard such a drastic initial reduction to be an important feature of my invention.

Another example of the teachings of this invention, as relating to titanium-clad iron bodies, is titanium cladding of aluminum and aluminum alloy bodies. The requirements leading to good results in cladding aluminum generally, are similar to those previously described in cladding iron. It is essential that the aluminum or aluminum alloy have about the same ductility and hardness as the iodide titanium to prevent rupturing of the titanium during the rolling process. Good results were obtained using Duralumin and magnesium aluminum alloys with similar ductility and hardness to titanium. Such a composite structure exhibits excellent characteristics for a wide variety of uses. By way of example, since titanium is generally not attacked by various foods, and since aluminum is an excellent heat conductor, pot, pans and food-containing utensils generally, represent but one of many applications. One preferred cladding method is descrbied in the following example. A sheet of Duralumin, ½ x 2 inch, in the "as received" condition was heated to about 500° C. in a hydrogen atmosphere and water quenched. The Duralumin sheet was then wire brushed on one side to remove the aluminum oxide coating. A titanium sheet also ½ x 2 inch was also wire brushed on one side. The titanium sheet was 0.050 inch thick and the Duralumin sheet was 0.062 inch thick. The wire brushed surfaces of the titanium and the aluminum sheets were then placed in contiguous relationship,

the outer surfaces coated with $Mg(OH)_2$ in water as previously described in the iron cladding method, and passed through a pair of 10 inch diameter reduction rolls for an overall thickness reduction of about 40%. Rolling velocity was 100 feet per minute. After the first draft of about 0.050 inch, the two strips were found to be firmly bonded together and capable of further mechanical working. The final thickness of the titanium aluminum composite structure was about 0.055 inch. Of this thickness, 0.030 inch represented titanium. A second draft of the joined sheets of about 0.020" resulted in some overworking of Duralumin at the edges of the strip but the remainder was firmly bonded. While a 30% initial reduction is sufficient as a minimum, initial reduction of 40 to 50% is more satisfactory for aluminum and titanium.

Duralumin is a trade name applied to the first aluminum-copper-magnesium type of age hardenable alloy (17S), which contains nominally 4% Cu., ½% Mn and ½% Mg. It is commercially available as Duralumin.

The above example was also employed in cladding a magnesium aluminum alloy, MgAl, commercially available and referred to as $6061T_6$ containing:

0.4–0.8% Si, 0.7% Fe, 0.15–0.40% Cu, 0.15% Mn, 0.8–1.2% Mg, 0.15–0.35% Cr, 0.25% Zn, 0.15% Ti, 0.05–0.15% impurities,

and the remainder aluminum.

A further method of cladding using press apparatus employed the same process as given in the above example with a sample of titanium of 0.004 inch thick and 2S (commercially pure) aluminum 0.010 inch thick. Instead of passing these sheets through rolls, they were placed in a hydraulic press and pressure of about 100 tons per square inch exerted thereon. After application of this pressure, the titanium and aluminum were bonded as a composite structure.

It is preferable to anneal the composites before further mechanical working. Stress relieving by heating to 300° C. gives good results.

I have, therefore, discovered that metallic titanium may be clad on a different metal base by cold-rolling provided the titanium will weld under plastic deformation to the base metal and further, that the ductility of the titanium is sufficient to permit its plastic deformation at a rate compatible to the deformation of the base metal. Further, the titanium should work harden at approximately the same rate as the base metal so that the two metals continue to elongate at about the same rate during all stages of working. The foregoing explanation advanced for the behavior of titanium with respect to cold roll cladding is intended to express a probable theory and should be regarded as such.

From the foregoing, it is apparent that I have discovered a practical method of applying an adherent, continuous coating of titanium on a different metal base by cold rolling, and more particularly, I have succeeded in producing cold-rolled iron strip material having a coating of metallic titanium. I have also discovered a novel, practical means of fabricating formed structural elements composed of thin titanium.

The specific examples have been set forth as illustrative of the invention, it being understood that many changes and modifications may be made without departing from my invention in its broader aspect, and I aim, therefore, in the appended claims to cover all such changes and modifications as fall within the true spirit and scope of my invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method of forming a thin-walled titanium article comprising in combination, utilizing a thin sheet of high-purity titanium of at least about 99.9% titanium and a sheet of metal taken from the group consisting of iron and aluminum, cleaning at least one surface of each of said sheets to remove foreign matter, placing the sheets in assembled relationship with the cleaned surfaces in contact with each other, effecting at least a 30% cold reduction in the thickness of the joined sheets by running them through opposed rolls to bond said sheets continuously over their cleaned and engaging surfaces to thus unite the sheets into an integral body capable of withstanding further mechanical working and remaining integral, forming the joined sheets by further mechanical working into a configuration other than sheet form, and thereafter removing the other metal from the titanium.

2. A method of forming a bond between a sheet of titanium and a sheet of metal taken from the group consisting of iron and aluminum comprising, selecting a relatively thin titanium sheet of a purity of about 99.9% titanium and a sheet of metal from said group having similar work hardening and ductility characteristics to that of titanium, cleaning a portion of each of said sheets to remove foreign matter, placing the cleaned portions of said sheets in assembled and contiguous relationship, effecting at least a 30% cold reduction in the combined thickness of the joined sheets in one pass through a rolling mill to provide a bond extending substantially continuous between the cleaned and engaging portions so that said sheets become integral and capable of withstanding a further mechanical working while remaining integral.

3. The method as described in claim 2 as applied to bonding of titanium and aluminum.

4. The method as described in claim 2 employed to bond titanium and an aluminum alloy.

5. The method as described in claim 2 wherein said 40% reduction is accomplished in a press apparatus instead of a rolling mill.

6. A method of forming a bond between a relatively thin sheet of titanium and a relatively thin sheet of iron comprising utilizing said sheet of titanium of at least 99.9% titanium, cleaning at least one surface of each of said sheets to remove foreign matter, placing the said sheets in assembled relationship with the cleaned surfaces in contact, and effecting at least 30% cold reduction in the thickness of the joined sheets by running them through opposed rolls to provide a bond between said sheets extending continuously over the cleaned portions in engagement so that said sheets are united into an integral bond capable of withstanding further mechanical working and remaining integral.

UNITED STATES PATENTS

References Cited in the file of this patent

2,691,815 Boessenkool ---------- Oct. 19, 1954