United States Patent Office

3,060,557

Patented Oct. 30, 1962

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3,060,557

METAL CLADDING PROCESS AND PRODUCTS RESULTING THEREFROM

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No Drawing. Original application Mar. 25, 1957, Ser. No. 647,973, now Patent No. 2,985,955, dated May 30, 1961. Divided and this application Mar. 24, 1961, Ser. No. 98,006

2 Claims. (Cl. 29—194)

This invention relates to a method of cladding one metal with another and to the products resulting from such method and more particularly the instant invention relates to a cladding method in which an intermediate metal is, or intermediate metals are, interposed between the base metal and the cladding metal, such interposed material acting as a diffusion barrier to eliminate the formation of brittle and continuous intermetallic compounds between the base and the cladding metal.

This application is a divisional application of Serial No. 647,973 filed March 25, 1957, now U.S. Patent No. 2,985,955.

An object of the instant invention is to provide a method whereby hithertofore impossible permanent metal cladding may be performed, the end product of such cladding procedure being extremely stable and not subject to separation during forming operation or in service.

Another object of the instant invention is to provide a metal cladding process whereby the clad metal will be strongly adherent to the base metal and where the formation of continuous and brittle intermetallic compounds of the base metal and clad metal does not occur.

A further object of the instant invention is to provide a method of cladding one metal with another in a permanently bound union.

Still another object of the instant invention is to prevent the formation of continuous and brittle intermetallic compounds between the base metal and the clad metal.

A specific object of the instant invention is to provide a method whereby steel may be clad with titanium through the interposition of a vanadium diffusion barrier between said metals.

Other objects, features and advantages of the instant invention will become apparent to those skilled in this art from the following disclosures thereof.

Many attempts have been made to clad one metal with another with varying degrees of success. Such processes and end products have assumed a greater importance in present day technology with the existence of extremely severe operating conditions. It has become desirable to combine the cheapness of base metals such as steel with highly corrosion resistant but expensive metals, for example, titanium, in order to be able to utilize the advantages of each. In some cases cost is not the important factor, for two expensive metals may be united to have the beneficial attributes of each of the finished product. It is well-known in the art and we have found in our experiments that in many cases it is impossible to form durable clads, particularly when the metals are used or treated under high temperature conditions and when continuous and brittle intermetallic compounds of the two metals are formed.

It is known that titanium has excellent corrosion resistance in sea water and various chemical environments. Unfortunately, the high cost of the metal precludes its use in many potential applications. By the use of the instant invention titanium may be clad onto steel and the ratio of titanium to steel is quite small. Thus, steel

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is the load sustaining member, while the corrosion resistance of titanium is fully utilized.

When the attempt is made to clad for example titanium onto steel, although the titanium will adhere at low temperatures, this is not the case after annealing and subsequent circumstances where the clad is subjected to stress, as for example, by bending or other fabrication procedures. At high temperatures, or under physical stress, the titanium will separate from the steel and result in the destruction of the usefulness of the clad. Once the titanium and iron have separated, not only may the structural element of which they are a part be vitally impaired, but also the steel is no longer afforded the protection of the titanium and becomes subject to corrosive influences and the like.

This problem of separation of the clad metal from the base metal is not limited to the titanium and steel system, but as we and others have found, may occur in practically every case in which the two metals form continuous and brittle intermetallic compounds at their interface. As the intermetallic compounds are formed, embrittlement of the joint or weld occurs.

The instant invention may be utilized in all cladding systems where continuous and brittle intermetallic compounds are normally formed at the interface of two metals. The basic concept underlying our invention is the fact that a third metal may be interposed between two other metals to firmly clad these two other metals if the intermediate metal does not form continuous and brittle intermetallic compounds with either the clad or the base metal. Using the titanium-steel example, once more we see the following: at room temperatures unstressed titanium clad steel is stable and will not separate, form intermetallic compounds, or become brittle. However, as the temperature of the bimetal is increased the intermetallics form by diffusion a continuous intervening layer with subsequent embrittlement. If a thin sheet of vanadium is inserted between the titanium and steel and then the tri-layered mass heated and compressed to form the finished products, the material will be extremely stable at elevated temperatures and there is no harmful formation of intermetallic compounds with the consequence involved therein. This phenomenon is explained by the fact that vanadium does not form continuous brittle intermetallic layers with either titanium or iron and therefore acts as a diffusion barrier between the two metals. The utilization of a diffusion barrier metal is novel and the teachings of the instant invention make it readily used in a broad variety of cladding materials.

Since the use of a diffusion barrier metal as a preventa-of harmful intermetallic compound formation is basically the heart of the instant invention, we feel it necessary to elaborate upon the principle which determines the correct material to use. The most important limitation, of course, is that the interposed material be unable to form continuous and brittle intermetallic compounds with either the base or the cladding metal. If this formation is not possible the result will be no embrittlement and no separation of the metals during subsequent forming or in service.

To illustrate, let us assume that we wish to clad metal A with metal C and that the harmful intermetallic compound A_xC_y may be produced. Let us now interpose metal B between A and C, and heat and press or roll the mass together to form a clad material. In this case metal B bonds with both metal A and metal C and the interfaces present stably welded structures.

A great deal of the work which led to the instant invention was concerned with the cladding of steel with titanium. We found that the mere use of these two metals, while stable at room temperature, became practically useless at an elevated temperature or after annealing. We found continuous intermetallic compound formation and embrittlement at the interface of what was once, at least to all outward appearances, a durable joint. We then interposed a thin sheet of vanadium between the two, formed it in the exact same way that the titanium-steel combination per se was formed and then found that an extremely stable material resulted. This material did not separate on bending or become brittle at elevated temperatures.

Pure metals each have their own intrinsic crystal structure and physical properties. The simplest alloys are microscopically fine mixtures of the pure metals or solid solutions thereof. It frequently happens that the alloy of two pure metals at some simple ratio of atomic concentrations contains neither of the pure metals in their free form. The alloy has a new crystal structure unlike either of the parent metals, has quite different physical properties and is almost invariably brittle and is called an intermetallic compound or an intermediate phase.

If one examines all of the possible alloys in a simple alloy system, the sequence of structures with increasing alloy may be:

(*a*) pure metal A
(*b*) a solid solution range of B in A
(*c*) a mixture of solid solution A with compound A_xB_y (x, y are integers)
(*d*) pure intermetallic compound A_xB_y
(*e*) a mixture of A_xB_y with solid solution B
(*f*) a solid solution range of A in B
(*g*) pure metal B.

We have found that many other systems are well adapted to this method of cladding. Some of these systems are as follows:

Clad Metal	Diffusion Barrier Metal	Base Metal
Zr	Ti+V	Fe
Zr	Ti	V
Mo	Cu	Fe
Mg	Ti	Th
V	Mg	Be
Ti	V+Cu	Ni
Ta	V	Fe
Be	Mg	V
Al	Be+Mg	Fe
Ta	Ag	Cu

It should be understood that the terms "Clad Metal" and "Base Metal" used in the above chart may be interchanged, depending upon which metal is considered the clad. Thus, for example, if it were necessary to use zirconium as the base metal, iron could be clad thereon by the interposition of a layer of titanium and a layer of vanadium therebetween.

A diffusion barrier consisting of two or even more metals should be next considered. Such a quadripartite cladding system must be used when a single known interposed metal which forms harmful intermetallics with neither the base now the clad cannot be found. Consider the example of aluminum-beryllium-magnesium-iron in either cladding aluminum to iron or vice versa. Aluminum forms intermetallics with iron with the end result that these materials will separate when heated and bent. If beryllium alone is interposed between the aluminum and iron, the clad will also fail, failure occurring at the beryllium-iron interface since these two metals form intermetallics. The aluminum-beryllium interface will remain stably united since these metals do not form intermetallics. The problem thus is one of using the correct metal between the beryllium and iron layers, by correct, of course, is meant one not forming harmful intermetallics with either. Magnesium admirably fulfills these requirements. It is seen that not only must the proper metal be selected, but its correct positioning in the system must be maintained. In the example given above, if the position of the magnesium and beryllium were reversed, the end product, say of aluminum-clad-iron would not have the desirable properties afforded by the instant invention.

As above stated, it is quite feasible to clad steel with titanium by interposing a thin sheet of vanadium between the two metals. We have also found that the system comprising: titanium-vanadium-copper-steel is also conveniently used for this desirable end product. The various interfaces of titanium-vanadium, vanadium-copper, and copper-iron do not give rise to any intermetallic compounds.

A roll clad operation is normally performed by laying a slab of one metal on top of the other. Such composite is usually first welded around the edges to prevent relative movement and to exclude air and then the unit is hot rolled using very large reductions per pass. This results in the development of a pressure weld between the two metals. The pressure weld must be of sufficient strength to tolerate bending of the clad without separation. If this simple rolling operation is performed on a composite titanium and steel unit, it is possible to bond the two metals. However, the result and clad, after annealing, cannot tolerate bending operations such as are needed to fabricate the clad into some useful form. Continuous brittle intermetallic compounds form at the interface through interdiffusion to negate the sought desirable end product.

In order that our process may be fully understood, the following detailed example is presented:

Example 1

Titanium sheet and steel sheet, 0.125 and ¾ inch thick respectively were selected as the cladding and clad materials. The relative thickness of the starting materials will be the same in the finished product. Ductile vanadium sheet of practically any thickness is interposed between the titanium-steel interface. Thickness of 0.025 and 0.050 inch have been successfully utilized. The steel may be of either the plain carbon or the stainless variety. The initial "sandwich" assembly must preclude the admission of air during rolling, for both vanadium and titanium are quite reactive with various components of air at the rolling temperature. This exclusion is most conveniently accomplished by welding the vanadium to the titanium and the vanadium to the steel, being careful not to form a titanium-steel fusion bond. Another air exclusion method is to form a cavity in the steel for the insertion of the vanadium and titanium covering with a steel plate and welding shut. After the sandwich is formed, hot rolling is performed in the usual manner. Rolling is performed at a temperature range from about 750° to 1000° centigrade. The thickness reduction per rolling pass seems to be no consequence. Experiments were run where reductions of 0.025 and 0.100 inch per pass yielded clads of similar quality. The minimum reduction for bonding seems to be about 60%, although the quality of the clad may not be very good until a reduction of near 80% has been accomplished. Even greater reductions (80–95%) have provided better clads.

The above example introduces a diffusion barrier which prevents the formation of damaging brittle intermetallic compounds. However, due to the carbon content of the steel, there is apparently some formation of discontinuous complex carbides. This carbide formation does not seriously affect the bend ductility of the clad or the stability of the interface union. We have found that it is possible to prevent the formation even of these carbides by the use of a second intervening layer, such layer being of pure copper. The fabrication of such a four-tiered clad is the same as that for the tripartite material discussed above. The copper sheet is interposed between the steel and vanadium of Example I. Copper sheet 0.007 inch thick was employed, it of course being understood that here again varying thickness may be utilized.

It will be understood that modifications and variations may be effected without departing from the spirit and scope of the instant invention.

We claim as our invention:

1. Titanium clad steel having interposed between the said titanium and the said steel and metallurgically bonded to both said titanium and said steel a diffusion barrier metal to prevent the formation of intermetallic compounds of the titanium and steel, said diffusion barrier metal being vanadium.

2. Titanium clad steel having interposed between said

titanium and the said steel a diffusion barrier to prevent the formation of intermetallic compounds of the titanium and steel, said diffusion barrier being a layer of vanadium and a layer of copper, said vanadium layer positioned between the titanium and the iron, and the said copper layer being positioned between the vanadium and steel layers, the interfaces of all of said metallic constituents being metallurgically bonded one to the other.

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