# United States Patent

[11] **3,604,103**

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[21] Appl. No. **538,538**
[22] Filed **Mar. 30, 1966**
[45] Patented **Sept. 14, 1971**
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## [54] METHOD OF CLADDING METALS AND COMPOSITES THEREOF

**10 Claims, No Drawings**

[52] **U.S. Cl.** .......... **29/472.3,** 29/504, 29/198
[51] **Int. Cl.** .......... **B23k 31/02**
[50] **Field of Search** .......... 29/198, 504, 472.3, 470.1, 497.5, 498

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**ABSTRACT:** A method of forming an integral metallurgical composite of dissimilar metals one of which is a refractory metal comprising covering the refractory metal with at least one other metal to form a pack, heating the pack and rolling the pack, the heating and rolling being carried out in an essentially inert atmosphere, preferably high purity argon, for a time and at a temperature conducive to achieving a diffusion bond between the metals and the desired combination of mechanical and physical properties of the composite.

# METHOD OF CLADDING METALS AND COMPOSITES THEREOF

This invention relates to a novel method of cladding dissimilar metals and particularly to a method of cladding dissimilar reactive metals by roll bonding in an inert environment and to composite articles made by the method.

In general, a reactive metal is a metal which reacts adversely with gaseous constituents in the atmosphere. Within the class of reactive metals is a group having a melting point greater than 3500° F. known as refractory metals. Refractory metals are highly reactive under normal atmospheric conditions and for this reason are extremely difficult to bond to nonrefractory metals and to each other. Basically, there are four commercial refractory metals: columbium molybdenum, tantalum and tungsten, although by definition the group also includes additional metals such as hafnium, rhenium, and their alloys. For the purpose of our invention, it is to be understood that the term reactive metals includes the refractory metals and alloys thereof.

It is well known that various combinations of mechanical properties can be obtained by alloying reactive metals. However, in order to achieve such properties, certain physical characteristics often desired in the resulting alloy must be sacrificed. Present design requirements for space vehicles and atomic power reactors require both qualified mechanical properties and required physical properties such as neutron absorption, emittance, heat capacity, corrosion resistance, resistance to gas contamination and thermal expansion. In these and other application, such parameters are critical to the success of the design and, hence, are of prime importance in determining the material to be used.

We have invented a novel method of cladding dissimilar reactive metals to each other to provide an integral composite which exhibits the required combination of mechanical and physical properties. Basically, our method comprises heating and rolling a preformed pack consisting of dissimilar reactive metals in an inert environment. The composite formed by our method can meet the properties required to fit design applications.

The bonding of dissimilar reactive metals to each other is made extremely difficult by the recognized susceptibility of these metals to react adversely with gaseous atmospheric constituents, thus preventing the formation of an integral bond at the interface between the metals. Accordingly, in bonding such metals it is paramount that gas-metal reactions be avoided. Through the use of a controlled inert atmosphere, such as high purity argon, we have invented a method by which reactive metals may be bonded readily and safely, with the resulting metallurgical composite being extremely useful in specialty and continuous large-scale operations and applications.

Heretofore, intensive work has been undertaken in the field of solid state diffusion bonding of dissimilar reactive metals. Investigators have found that an adequate intermetal bond can be obtained by heating the materials to be clad to high temperatures in vacuum of low partial pressures of air contaminants. The bond resulting from this method is not entirely satisfactory for any required further working of the bonded metals, since the structure of one or both of the component materials of the composite may be adversely affected as a result of the relatively long time exposure at temperatures required for solid-state diffusion bonding. Moreover, this bonding method requires highly expensive vacuum equipment and stringent controls which makes the operation impracticable for large scale operations.

Our novel method of bonding dissimilar reactive metals and the composites produced thereby has met with considerable success is shown hereinafter by the results of tests made on articles bonded by the method of our invention. We have provided a method by which dissimilar reactive metals can be successfully roll bonded, the bond being achieved being of the integrity and quality required for further fabrication and high temperature application.

By our method of bonding, we have been able to form an integral bond between various combinations of reactive metals. Particularly, we have clad one refractory metal to a second refractory metal, a refractory metal to a nonrefractory reactive metal and a reactive metal to a common metal, such as copper and steel. In all cases, the intermetallic bond achieved is characterized by strength and its opposition to decladding in subsequent testing and application.

In performing the method of our invention using two refractory metals, a base metal, such as molybdenum, and a cladding metal, such as columbium, are first thoroughly cleaned and properly positioned in surface contact with each other to form a mechanical composite or pack. Preferably, the base metal is sandwiched between two rectangular sections of the cladding metal, the edges of the cladding metal extending outwardly beyond the edges of the base metal. These exposed edges of the base metal are then covered with sections of cladding metal, such that the base metal is surrounded entirely by the cladding metal. By securing the adjacent edges of the cladding metal, as by tack welding, the base metal is held firmly within the cladding metal.

Alternatively, in the simplest embodiment of our invention, a base metal and a single cladding metal having the same outside dimensions can be used, with the ends of the dissimilar reactive metals being secured directly to each other. In such a construction, the cladding metal covers, but does not completely surround, the base metal. Moreover, if the surfaces of the metals to be bonded are clean and substantially free of faults, the metals need not be specially secured, provided the metals do not shift or separate in relation to each other during subsequent forming of the composite.

The pack thus formed is introduced into a heating furnace which is continuously supplied with high purity inert gas. We have achieved our best results in an atmosphere of essentially pure argon. Specifically, our work has been conducted in a sealed chamber filled with argon, and including a furnace and a rolling mill. By controlling the equipment from outside the sealed chamber, contamination of the atmosphere within the chamber is kept at a minimum. Inert gas is continuously fed directly into the furnace and into the chamber at the required rates. In practicing our invention, we have been able to supply to the furnace an inert atmosphere having a purity on the order of one part per million oxygen and one part per million moisture, although a decrease in this high degree of purity to that generally supplied to the chamber will not adversely affect the properties of the final bonded composite of our invention.

After the pack is heated to a temperature appropriate for hot working of the pack and conducive to achieving the desired mechanical properties, it is transferred immediately to the rolling mill located in the chamber adjacent the furnace. In the chamber, we have successfully roll bonded in argon atmospheres having as much as 5–10 parts per million oxygen and 12–30 parts per million moisture.

In practice, we have used a conventional two-high rolling mill wherein the heated pack is rolled to the desired total thickness required for specialty application or use in subsequent processes. While it may be preferable to reduce the pack thickness by reductions of 70–80 percent to obtain the desired area dimensions and the metallurgical benefits derived from hot work deformation of the materials, we have found that the reduction required to achieve a satisfactory bond by our method is less than that required in conventional methods of bonding using evacuated protective jackets.

Thus, the method of our invention provides an integral metallurgical bond between dissimilar reactive metals. The pack which has been formed with the reactive metals placed in surface contact during the heating and rolling process is maintained in an inert environment where it is heated and rolled. The heating and rolling temperatures employed are conducive to achieving the desirable properties of the selected combination of metals, and the completed metallurgical composite displays both satisfactory physical and mechanical properties. Roll bonding in an inert atmosphere, according to our invention, has been performed successfully at temperatures in excess of 3000° F. without the necessity for jacketing the pack, as is commonly done in bonding operations using other metals and alloys, or otherwise protecting the reactive metals from contamination.

Successful bonds have been obtained between a variety of dissimilar metals. The examples of test results discussed hereinafter were obtained from samples tested in their "as-rolled" condition without provision for optimum temperatures, reductions or heat treatments. It will be obvious to those skilled in the art that the bonding mechanism herein disclosed will be improved by exacting control of material reductions, in-process anneals, and the selection of dissimilar reactive metals having compliancy to bond to one another.

Photomicrographs taken of a molybdenum sample clad with columbium in accordance with our teachings, the initial rolling of the heated pack being made at a temperature of 1800°–2000° F., and tested at room temperature, indicated that the cladding was successfully achieved. Similarly, a molybdenum base alloy A having a nominal composition of 0.5 percent titanium, 0.10 percent zirconium and the balance molybdenum, bonded by our method to a columbium base alloy B having a nominal composition of 5 percent molybdenum and 1 percent zirconium, the balance being columbium, did not declad during test. The initial rolling temperature of the Alloy A/Alloy B pack was 1900°–2200° F. Tungsten clad with tantalum using our method with an initial rolling temperature of 1900°–210020 F., and tested at 400° F. showed no decladding or any separation at the interface of the dissimilar metals, nor was there any evidence of the formation of undesirable intermetallic structures. Likewise, tungsten clad with a tantalum alloy following the method disclosed herein, the initial rolling being made at a temperature of 2200°–2400° F., and then tested at 400° F., revealed a very satisfactory bond with no interface separation.

Data taken of tensile tests made on composites bonded by the method of our invention is shown in Table I.

TABLE I.—TENSILE TEST DATA

| Metals | Temperature, ° F. | UTS (×10³), p.s.i. | .2% YS (×10³), p.s.i. | Elongation, percent |
|---|---|---|---|---|
| Cb-Mo | [1] R.T. | 72.1 | 68.8 | 11.4 |
| | 1,000 | 45.8 | 45.7 | 4.7 |
| | 2,000 | 11.8 | 8.0 | 39.4 |
| Alloy A/Alloy B | R.T. | 110.6 | 97.3 | 18.4 |
| | 1,000 | 85.1 | 73.1 | 10.3 |
| | 2,000 | 56.9 | 49.2 | 24.2 |
| | 2,400 | 30.7 | 29.9 | 37.1 |
| Ta-W | R.T. | 84.5 | 79.6 | 6.2 |
| | 900 | 64.9 | 42.3 | 18.6 |
| | 2,000 | 28.3 | 25.2 | 11.9 |

[1] Room temperature.

From these results, it is apparent that an integral bond was achieved with the resulting composite exhibiting complimentary strength-ductility combinations; that is, the percent elongations of the composite were higher than those normally displayed by the less ductile metal in the composite and the strength exhibited was higher than that normally displayed by the lower strength metal.

Once an integral bond is established between the dissimilar reactive metals by our method, the composite may be hot or cold worked conventionally to achieve any required dimensional limits without destroying or weakening the intermetallic bond. For example, the columbium-molybdenum composite and the Alloy A/Alloy B composite, each having a total thickness of 0.050 inch after roll bonding in accordance with our invention and on which the tests of Table I were made, were processed to foil by cold rolling reductions and anneals with evidence of excellent ductility in the foil; the foil thickness tested was 0.002 inch columbium/molybdenum and 0.006 inch Alloy A/Alloy B.

Successful bonding of a number of dissimilar combinations of metals of commercial purity has been achieved in an inert environment by the method of our invention. For example, using an inert atmosphere of argon, we have bonded stainless steel to Alloy A; stainless steel to tantalum; stainless steel to a tantalum alloy; stainless steel to titanium; molybdenum to titanium; and copper to titanium.

In bonding certain of the dissimilar metals to each other, it has been recognized that the existence of low melting phases or brittle intermetallic structures between bonded metals adversely affect the physical and mechanical properties of these metals during bonding, heat treatment, fabrication or subsequent use. We have found, for example, that a roll bonded composite of austenitic stainless steel and titanium cannot be annealed in the 2050°–2150° F. temperature range necessary to obtain the required properties of stainless steel or of newly developed titanium alloys. Upon heating the composite in this temperature range, a severe reaction occurred whereby the titanium melted completely. By providing an interlayer or barrier material between the base metal and the cladding metal, these undesirable characteristics can be avoided in the final bonded composite. The barrier metal used should have mutual bonding characteristics with both the cladding and the base metals, or itself be a bonded composite of two in accordance with the present invention dissimilar metals, each of which has excellent bonding characteristics with its adjacent metal.

A composite made in accordance with our invention need not be limited to direct specialty application. The composite may be used as a filler material to facilitate the joining of much larger metal sections by some other joining method. As an illustration, the joining of large sections by diffusion bonding may be achieved at practicable temperatures and pressures by selection of a filler material composed of metals which would induce a favorable diffusion reaction with the surfaces of the large sections. The use of such filler material for lowering the temperatures and pressures required for diffusion bonding would, in general, obviate the need for specially designed, expensive equipment and high operating costs.

Objects of utilization for the composites of reactive metals provided by the method of our invention are many; all of the following and others are present and potential applications for the product of our invention:

Jet tubes and reentry cones require high temperature abrasion resistant surfaces on bulk material capable of withstanding thermal and mechanical shock at moderate and low temperatures The poor ductility at low temperatures of high temperature abrasion resistant tungsten can be supported by the ductility and shock resistance inherent in tantalum or its alloy.

While an alloy such as a columbium base alloy consisting of approximately 1 percent zirconium, the balance columbium, is highly resistant to corrosion by liquid metals, there is enough interstitial pickup at low atmospheric pressures to destroy its corrosion resistance. A thin cladding of molybdenum or tungsten has proven an excellent barrier against such contamination and has demonstrated feasibility for high temperature energy conversion systems for space application.

Molybdenum exhibits a very high modulus of elasticity, necessary in the development of structural components; however, it shows poor brazing characteristics. Molybdenum or molybdenum alloy foil clad with a thin layer of titanium or columbium, overcomes the objectionable brazing problems of the base metal.

Copper clad with refractory metals having good corrosion resistance in particular corrosive media is a solution to the problem experienced by the chemical industry which utilizes metals having good thermal and electrical conductivity properties in a corrosive environment. The same industry requires material having the corrosion resistance of a costly refractory metal along with the low cost, availability, and other desired characteristics of steel. Steel vessels lined with a refractory metal can be fabricated from refractory metal clad steel plate produced by our method.

Our invention promotes the action of reactive metal mechanisms conducive to reliable bonds; provides the control latitude necessary to achieve desired physical properties in a product without sacrificing the mechanical properties; permits continuous cladding and accommodates a variety of dimension and thickness ratios between dissimilar metals.

Further, our invention makes possible and commercially practicable the quality bonding of large sections of dissimilar metals by means of conventional steel mill rolling facilities.

While we have described preferred embodiments of our invention, it is to be understood that it may be otherwise embodied within the scope of the following claims.

We claim:

1. The method of forming an integral metallurgical composite of dissimilar metals one of which is a refractory metal and the other of which is a reactive metal in an essentially inert atmosphere, said method comprising:

A. Covering a first metal with a second dissimilar metal such that the opposing surfaces of said metals are in surface contact to form a pack;

B. Heating said pack in said atmosphere to a temperature conducive to achievement of the desired mechanical properties of said composite; and

C. Rolling said heated pack in said atmosphere to form a diffusion bond between said first and second metals to provide said integral metallurgical composite.

2. The method of forming an integral metallurgical composite as described in claim 1 wherein said reactive metal has a melting point greater than 3500° F.

3. The method of forming an integral metallurgical composite as described in claim 1 wherein at least one of said dissimilar metals is selected from the group consisting of columbium, tantalum, tungsten, molybdenum and alloys thereof.

4. The method of forming an integral metallurgical composite as described in claim 1 wherein said inert atmosphere is argon.

5. The method of forming an integral metallurgical composite as described in claim 1 including securing the edges of said metals to prevent separation between said first and said second metals.

6. The method of forming an integral metallurgical composite of dissimilar metals one of which is a refractory metal and the other of which is a reactive metal in an essentially inert atmosphere, said method comprising:

A. Covering a first metal with a barrier metal;

B. Covering said barrier metal with a second dissimilar metal such that the opposing surfaces of said first metal and said barrier metal and of said second metal and said barrier metal are in surface contact to form a pack;

C. Heating said pack in said atmosphere to a temperature conducive to achievement of the desired mechanical properties of said composite; and

D. Rolling said heated pack in said atmosphere to form a diffusion bond between said first metal and said barrier metal and between said second metal and said barrier metal whereby an integral metallurgical composite is formed.

7. The method of forming an integral metallurgical composite as described in claim 6 wherein said reactive metal has a melting point greater than 3500° F.

8. The method of forming an integral metallurgical composite as described in claim 6 wherein at least one of said metals is selected from the group consisting of columbium, tantalum, tungsten, molybdenum and alloys thereof.

9. The method of forming an integral metallurgical composite as described in claim 6 wherein said inert atmosphere is argon.

10. The method of forming an integral metallurgical composite as described in claim 6 and including, prior to covering said first metal with a barrier metal, forming a composite barrier metal by

A. Covering a first metal with a second dissimilar metal such that the opposing surfaces of said metals are in surface contact to form a pack;

B. Heating said pack in said atmosphere to a temperature conducive to achievement of the desired mechanical properties of said composite;

C. Rolling said heated pack in said atmosphere to form a diffusion bond between said first and second metals to provide said integral metallurgical composite; and

D. Orienting said composite barrier metal such that each of the dissimilar metals comprising the composite barrier metal is in surface contact respectively to each of the metals to be bonded and adjacent to that metal with which bonding capability exists.