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METHOD OF BONDING NON-METALLIC ARTICLES TO METALLIC BASES

Ben Matchen, Niagara Falls, Ontario, Canada

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This invention relates to the bonding of non-metallic refractory articles to supporting metallic bases and to the composite and integral articles thereby produced. More particularly, this invention relates to a method of bonding non-metallic refractory articles formed from borides, silicides and carbides to bases of metal stock such as iron or steel to provide composite articles wherein the desirable characteristics of the refractory material may be conveniently utilized.

The application of non-metallic refractory materials in various industrial processes is becoming more and more prevalent. Such materials as titanium diboride and zirconium diboride, for example, when used as cathodes in electrolytic cells, have shown distinct advantages over the standard iron cathode conventionally utilized. One specific application is the use of these materials in cells for the reduction of alumina to aluminum metal.

Titanium diboride, for example, when fabricated to certain specifications, is characterized by a high density (above 88 percent of its theoretical value), low electrical resistivity (less than 30 microhm centimeters), high strength (greater than 40,000 p.s.i. cross bending at room temperature), low solubility in molten aluminum and excellent resistance to the electrolytes such as cryolite used in aluminum cells. Zirconium diboride exhibits similar properties.

One major problem associated with the use of these materials is the cost of the materials themselves both in powder form and in fabricated shapes. The production of borides of high purity is expensive and fabrication into shapes necessitates the use of great degrees of heat and pressure because of the relative hardness and refractoriness of these materials. Cathodes for electrolytic cells are produced in the form of bars and range in size from about 2 to 8 inches in diameter and from about 18 to 24 inches in length, while the "working end" or tip portion actually in contact with the electrolyte is only about one-third of this length. The remainder of the bar extends from the working end and is connected to a source of electrical power.

It has been found that a considerable saving of expense in the production of cathodes may be achieved if only the tip, or that portion in or adjacent to the electrolyte bath is formed of the costly non-metal and the remainder formed of a cheaper metal stock such as iron or steel. Similar savings may be realized with bonding, for various purposes, of other non-metals such as refractory silicides and carbides to a metal stock. Prior attempts to produce welds between metals and non-metals have not proved practical in high temperature operations. It is important in many applications that the bond be as thin as possible and yet strong, be refractory at high temperatures, and have good electrical conductivity.

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It is therefore an object of this invention to provide a method of bonding a refractory non-metallic article to a supporting metallic base and the combined article thereby produced.

It is another object of this invention to provide a method for bonding articles formed from refractory borides, silicides or carbides to bases formed of metal stock such as iron or steel.

It is still another object of this invention to provide such a bond in which desirable electrical properties of the non-metallic article are maintained.

It is a further object of this invention to provide a bond which is refractory at high temperatures, for example, to at least 900° C.

It is a still further object of this invention to provide a material which will successfully produce such a bond.

It is still another object of this invention to provide a composite and integral electrode for electrolytic cells in which the working end or tip only is formed of a refractory non-metal such as titanium diboride or zirconium diboride.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has been found that the above objects may be attained by bonding a refractory non-metallic article to a base of metal stock by a method known as high temperature brazing. High temperature brazing is a relatively new process. Theoretically, the brazing material should successfully bond itself to both the metal and non-metal. The interface between metal, non-metal and braze need not exceed more than a few microns in thickness. The bonding is thought to take place in a diffusion interface and presumably a new phase is formed in this region. This very thin diffusion or reaction zone of high temperature brazing is dissimilar to that of arc welding which depends on a relatively thick zone of braze penetration to effect a good weld.

The unique process which produces a metal to non-metal weld requires a correct choice of braze in order to "wet" or dissolve the two materials and at the same time maintain desirable strength and resistance. There is also some evidence that properties of the non-metallic article, i.e., porosity, thermal expansion, grain size, etc. may have an equally important role in producing a successful weld.

More particularly, the non-metal is provided in a desired form or shape. The method of fabricating the non-metal may be varied, and this affects the density and, in turn, the properties of the weld region. In the case of borides, for example, articles formed by cold-ramming and sintering have a density from 65 to 80% of theoretical and those formed by flexible-molding and sintering have a value from 70 to 85% of theoretical density.

Pieces hot-pressed from a raw mix will have a density from 85 to 95% of theoretical, while those hot-pressed from the boride will reach a value of from 90 to 98% of theoretical density.

Density is important in that the non-metal will become more impregnated by the braze if it is more porous. It should be stressed, however, that satisfactory welds are obtained according to the method of this invention regardless of density of the non-metal.

The surfaces of the refractory non-metal article to be welded are cleaned to free it of dirt and other foreign matter. Although a piece having freshly cut or ground surfaces at the location of the joint is preferred, good welds may be obtained where the piece has a clean "mold" surface. When articles of relatively high density are used, a slight burring of the surface to be welded is preferable to secure the best weld.

The base of metal stock is preferably modified to provide an end portion having increased contact area. The preferred modification includes a generally cup-shaped end portion. Other forms include "ball joints" or angular joints. In the preferred form, the non-metal piece is placed in the cup whose inside surfaces have been freshly machined and cleaned with an organic solvent to remove traces of grease or oil. A metal powder brazing mixture is placed under the non-metallic piece and in the annular space between the piece and the cup. This assembly is heated in a furnace, such as a molding furnace which provides a non-oxidizing atmosphere. As an add-

welded to metal stock in a similar manner. Also, while the following examples illustrate welding a non-metal to steel, almost any metal stock may be used.

The braze composition should preferably have a lower melting point than the metal stock. If it does not, the following method may be used to weld a non-metal to a metal having the same refractoriness as the braze. The non-metal piece is joined to the braze held in a container having a higher melting point than the braze. The outer material is then machined off leaving the non-metal firmly attached to the braze. The braze end is then joined to the metal stock in a manner well-known in the art.

In the following examples, and throughout the specification and claims, all parts are parts by weight unless otherwise specified.

Examples 1-6 illustrate the method of this invention when applied specifically to titanium diboride. A copper/manganese braze has been found successful in welding this non-metal. A composition of 60% copper and 40% manganese gives especially satisfactory results and with the addition of titanium hydride or titanium diboride the braze more readily dissolves the titanium diboride. The boride then recrystallizes in the braze forming numerous well formed crystals. In these examples, the assemblies of diboride members and steel members, having the brazing compositions noted interposed therebetween, were heated in an induction or molding furnace in a non-oxidizing atmosphere for 15 to 60 minutes at the temperatures indicated.

EXAMPLES (TiB₂)

	1	2	3	4	5	6
Braze Composition:						
Copper, percent.....	60.....	50.....	55.....	55.....	55.....	75.....
Manganese, percent.....	40.....	50.....	37.....	37.....	37.....	10.....
Nickel, percent.....						10.....
Cobalt, percent.....						5.....
Titanium hydride, percent.....			8.....	8.....	8(T25S).....	
Titanium diboride, percent.....					1,100 (A).....	1,250 (A).....
Temperature (° C.).....	1,150 (A).....	1,150 (A).....	1,100 (A).....	1,100 (A).....	1,100 (A).....	1,250 (A).....
Time at Temp.....	1 hr.....	1 hr.....	15 min.....	1 hr.....	15 min.....	1 hr.....
Diboride Rod:						
Rammed, sintered.....	X.....	X.....	X.....	X.....	X.....	X.....
Hot pressed.....						
Flexible mold sintered.....						
Grain size (mm.).....	1 to 2.....	1 to 2.....	.03 to .08.....	.03 to .08.....	.03 to .08.....	.01 to .05.....
Resistivity (microhm-cms.).....	N.D. (~100).....	N.D. (~100).....	13.0.....	22.....	22.....	25.1.....
Density (percent of theoretical), percent.....	~65.....	~65.....	93.4.....	90.2.....	90.2.....	78.4.....
Boundary:						
Thickness (mm.).....	.05 to .1.....	.03 to .05.....	<.01.....	<.01.....	.01.....	.08.....
Diboride solubility.....	Slight to moderate.....	Slight to moderate.....	Extreme.....	Extreme.....	Extreme.....	Slight.....
Resistivity (microhm-cms.).....	N.D.....	N.D.....	51.....	51.....	61.....	86.....
Weld Evaluation.....	Good.....	Good.....	Good.....	Good.....	Good.....	Fair.....

(A)—Argon atmosphere.
N.D.—Not determined.

ed precaution, inert gas, such as argon, may be fed into the furnace during the welding and cooling periods.

Several braze compositions have been successfully utilized in the method of this invention including brass, bronze, copper/manganese, copper/nickel, copper/manganese/nickel, copper/manganese/nickel/cobalt, nickel/boron and copper/nickel compositions with small amounts of titanium hydride or titanium diboride. The preferred composition is that of copper/manganese in proportions ranging from equal amounts of each metal to 70% copper and 30% manganese. Good welds are also achieved with several of the other compositions, especially those containing small amounts of titanium hydride or titanium diboride when a titanium boride piece is being welded. The copper/nickel compositions are not as effective in wetting the non-metal. However, higher brazing temperatures will somewhat obviate this deficiency.

The chemical composition of the non-metal may also be varied. Successful experiments have been conducted utilizing pieces of titanium diboride, zirconium diboride, zirconium diboride/5% chromium and molybdenum disilicide. Other refractory silicides and carbides may be

Examples 7-12 illustrate the method of this invention when bonding zirconium diboride. Successful welds of this non-metal to steel were characterized by two types of boundaries: (1) a relatively thick zone of braze penetration with solution and penetration of braze and diboride, and (2) a very narrow and sharp boundary between the braze and diboride. A new phase, bronze in color, was observed at the contact of diboride and braze and was interpreted as a fine-grained diffusion zone. While these two different conditions were observed in brazes of nearly identical composition, a possible cause for the thicker zone of braze penetration may be increased porosity of the diboride rod.

The solubility of zirconium diboride in all cases appeared to be less than that of titanium diboride in the braze. Hydrides and borides were not added to these brazes, hence no information on their effect was available. A braze composition of from 60-70% copper and from 40-30% manganese gave good results. In Examples 7-12, the assemblies were heated in a non-oxidizing atmosphere in an induction or molding furnace at 1150° C. for from about 60 to 120 minutes.

EXAMPLES (ZrB₂)

	7	8	9	10	11	12
Braze Composition:						
Copper, percent	60	60	60		65	70
Manganese, percent	40	40	40		25	30
Nickel, percent				84	10	
Boron, percent				16		
Temperature (° C.)	1,150 (A)	1,150 (A)	1,150 (A)	1,150 (A)	1,150 (A)	1,150 (A)
Time at Temp., hrs.	1	1½	2	2	2	1
Diboride Rod:						
Hot pressed	X					
Flexible mold, sintered		X				
Grain size (mm.)	.03 to .06	.01 to .02	.08 to .18	.05 to .15	.1 to .3	X
Resistivity (microhm-cms.)	23.7	15.2	14.0	14.0	14.0	.03 to .04
Density (percent of theoretical), percent	96	81	71.8	71.8	71.8	9.9
Boundary:						93
Thickness (mm.)	.02 to .04	.04 to .06	.12 to .34	.06	.15	.01
Diboride solubility	Slight	Some	Much	Slight	Slight	Slight
Resistivity (microhm-cms.)	N.D.	5	N.D.	N.D.	N.D.	N.D.
Weld Evaluation	Good	Good	Good	Fair	Fair	Good

(A)—Argon atmosphere.

N.D.—Not determined.

*—This rod contained 5 percent chromium.

In welding diboride bars, in many cases where brazes of copper and manganese are used, there is a contact reaction with the diboride involving a "plating" of copper-like metal on the outer edges of the diboride grains at the contact. This condition, however, has not been noted within the diboride member. It is possible this feature has a beneficial influence on resistivities of the welded pieces.

High temperature brazing of molybdenum disilicide was investigated because of its potential refractory applica-

EXAMPLE 13

A rod of molybdenum disilicide was welded to steel. The braze composition was 60% copper and 40% manganese and the brazing was conducted in an argon atmosphere in a molding furnace at 1150° C. for one hour and 30 minutes. The braze readily dissolved the disilicide and produced a good weld. The boundary consisted of a transition area nearly one millimeter in thickness. Various concentrations of recrystallized molybdenum disilicide and braze were observed in at least four zones in the transition area. The outline of the disilicide and transition zones in the braze were irregular due to extensive solution of the disilicide. The grain size of molybdenum disilicide in the bar was very fine, approximately 20 microns with a few grains somewhat larger in size. Some of the recrystallized disilicide grains in the transition zones were 2-3 times larger than those in unaffected regions.

While in the above examples, temperatures between 1100° and 1250° C. are indicated, temperatures ranging from 975° to 1300° C. are operable. The assemblies are heated at temperature for from 1 to 120 minutes, and preferably for from 1 to 15 minutes. The shorter times are, of course, preferred because of the economics involved. A few welds have been made at temperature for only one minute and appeared comparable to those made for longer time intervals.

What is claimed is:

1. A composite article comprising a titanium diboride member brazed to a steel member with a brazing composition containing from 50 to 70% copper, from 25 to 40% manganese and from 0 to 10% nickel.

2. A composite article comprising a titanium diboride member brazed to a steel member with a brazing composition containing about 84% nickel and 16% boron.

3. A composite article comprising a titanium diboride member brazed to a steel member with a brazing composition containing from 50 to 75% copper, from 10 to 50% manganese, from 0 to 10% nickel, and from 0 to 15% cobalt.

4. A composite article comprising a titanium diboride member brazed to a steel member with a brazing com-

position containing about 55% copper, 37% nickel and 8% of a member selected from the group consisting of titanium hydride and titanium diboride.

5. A composite article comprising a refractory non-metallic member selected from the group consisting of zirconium diboride, titanium diboride and molybdenum disilicide brazed to a conductive metallic member with a brazing composition selected from the group consisting of brass, bronze, a mixture consisting essentially of a major proportion of nickel and a minor proportion of boron and a mixture consisting essentially of from about 55 to 90% copper, from 0 to 50% manganese, from 0 to 30% nickel, from 0 to 15% cobalt, from 0 to 8% titanium hydride and from 0 to 8% titanium diboride.

6. The composite article of claim 5 wherein the brazing composition is about 60% copper and 40% manganese.

7. The method of bonding a refractory non-metallic member selected from the group consisting of zirconium diboride, titanium diboride, and molybdenum disilicide, to a metal member which comprises forming an assembly by interposing between the surfaces of said members to be bonded a brazing composition in the solid state selected from the group consisting of brass, bronze, a mixture consisting essentially of a major proportion of nickel and a minor proportion of boron, and a mixture consisting essentially of from about 55 to 90% copper, from 0 to 50% manganese, from 0 to 30% nickel, from 0 to 15% cobalt, from 0 to 8% titanium hydride and from 0 to 8% titanium diboride, heating the assembly in a non-oxidizing atmosphere to melt the brazing composition, and cooling said assembly to provide a bond between said members.

8. A method according to claim 7 in which said brazing composition in the solid state is in the form of a powder.

9. A method according to claim 7 in which said metal member is steel and the bonding is carried out at a temperature between 975° and 1300° C. for from 1 to 120 minutes.

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