April 14, 1964 J. H. WESTBROOK ETAL 3,129,070

METALLIC BOND

Original Filed Sept. 2. 1960

Fig. 1.

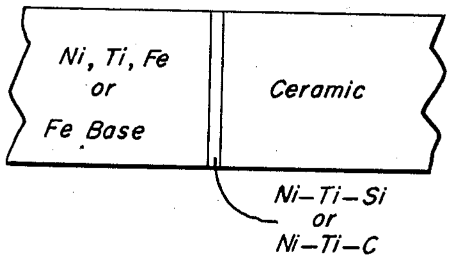


Fig. 2.

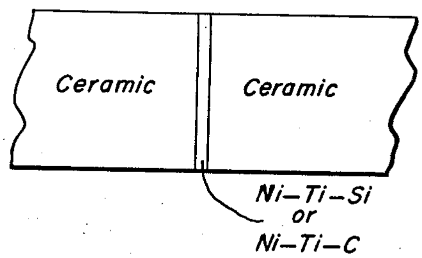
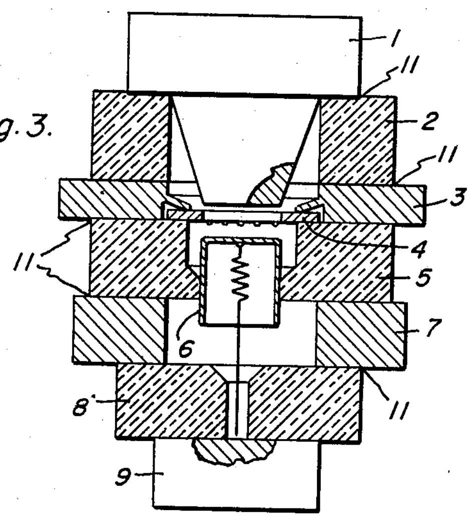


Fig. 3.



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METALLIC BOND

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Original application Sept. 2, 1960, Ser. No. 53,652, now Patent No. 3,091,028, dated May 28, 1963. Divided and this application Nov. 20, 1962, Ser. No. 238,991
3 Claims. (Cl. 29—195)

The present invention relates to articles bonded together by an alloy of nickel, titanium, and an element selected from the group consisting of silicon and carbon.

This application is a division of our co-pending application filed September 2, 1960, as Serial No. 53,652, now U.S. Letters Patent 3,091,028, issued May 28, 1963, and assigned to the same assignee as the present application.

One solution to bonding non-metallic refractory members together or to metallic members has been advanced by James E. Beggs in his patent for Metallic Bond, No. 2,857,663, patented October 28, 1958, and assigned to the assignee of this invention. In accordance with the method described in this patent, a metal member and a non-metallic body are placed in a stack with a metal shim member interposed therebetween, one of the members consisting essentially of a meal selected from the group consisting of titanium, zirconium, hafnium, thorium and alloys of more than one metal of the group and the other metal member consisting of a metal selected from the group consisting of copper, nickel, iron, molybdenum, chromium, platinum, cobalt, and alloys of more than one metal of the group. The stack is heated in a non-reactive atmosphere to a temperature at least equal to the melting point of the eutectic alloy of the metal member and the metal shim member and below the melting point of both these members to form in place a molten reactive alloy which wets the non-metallic refractory body. The stack is then cooled to provide a bond capable of withstanding a temperature substantially equal to that at which the bond was formed.

Even when this method is used, it is possible for one or more of the intermetallic compounds to form of the formula types Ti_2M, TiM, or TiM_3 where M is iron, nickel or cobalt. Formation of such binary compounds results in a brittle and weak layer in the bond and might, therefore, be a source of weakness in the brazed bond. Thus, it is desirable to have a metallic bond in which the formation of such brittle intermetallic titanium alloy is avoided or in which the adverse effects of their presence are alleviated by the concomitant formation of a tough intermediate layer.

It is an object of our invention to provide an article bonded together by an alloy of nickel, titanium and an element selected from the group consisting of silicon and carbon.

It is another object of our invention to provide an article comprising a metal portion and a non-metallic refractory portion bonded together by an alloy of nickel, titanium and an element selected from the group consisting of silicon and carbon.

It is a further object of our invention to provide an article comprising non-metallic refractory portions bonded together by an alloy of nickel, titanium and an element selected from the group consisting of silicon and carbon.

In carrying out our invention in one form, an article comprises a metal portion selected from the group consisting of nickel, titanium, iron and iron base metals, a non-metallic refractory portion, and an alloy of 50 to 55 atomic percent titanium, 0.3 to 10 atomic percent of an element selected from the group consisting of silicon and carbon, and the balance being nickel bonding said metal portion to said non-metallic refractory portion.

These and various other objects, features and advantages of the invention will be better understood from the following description taken in connection with the accompanying drawing in which:

FIGURE 1 is an illustrative example of an article which may be formed by our invention which employs a metal portion of titanium, nickel, iron or an iron base metal;

FIGURE 2 is an illustrative example of an article that may be formed by our invention in which two non-metallic refractory bodies are bonded together by employing an interposed alloy consisting of nickel, titanium and an element selected from the group consisting of silicon and carbon; and

FIGURE 3 is a partial sectional view of a miniature vacuum tube constructed in accordance with our invention.

We discovered unexpectedly that alloys consisting of nickel, 50 to 55 atomic percent titanium, and 0.3 to 10 atomic percent of an element selected from the group consisting of silicon and carbon produced strong metallic bonds between non-metallic refractory bodies as well as between refractory bodies and metal members. We found further that these alloys formed liquid phases at temperatures in the range of 950° C. to 1200° C. As cast, such compositions possess unusual ductility and strength despite the fact that microstructurally they consist of an agglomeration of two or more intermetallic compound phases with no pure metal present. Therefore, it does not appear necessary to have a truly single phase miscrostructure to achieve a significant amount of toughness.

During the research which led to the discovery of these alloys of nickel, titanium and an element selected from the group consisting of silicon and carbon, a series of small arc melted buttons were prepared. Typical compositions in atomic percent were as follows: 39.6 Ni–54.2 Ti–6.3 Si, 47.9 Ni–50.0 Ti–2.1 Si, and 47.9 Ni–50.0 Ti–2.1 C.

One of these buttons was found to have an impact strength of 14 inch pounds in a standard National Advisory Committee for Aeronautics drop weight impact test. After annealing this composition for 100 hours at 950° C., the resulting coalesced structure consisting of a matrix of one intermetallic compound and a small volume fraction of another ternary silicide showed considerable ductility in a room temperature bend test. The subject alloy exhibited a proportional limit of 38,000 pounds per square inch and a modulus of rupture of 105,000 pounds per square inch.

In FIGURE 1 of the drawing, a titanium, nickel, silicon, iron or iron base metal member or portion may be bonded to a non-metallic refractory body or portion by placing between the portions an alloy of nickel, 50 to 55 atomic percent titanium, and 0.3 to 10 atomic percent of an element selected from the group consisting of silicon and carbon. For example, a titanium tube member may be bonded to a ceramic tube body by placing such an alloy shim between the portions. This stack is then held in contact and heated to the melting point of the alloy which is in the temperature range of 950° C. to 1200° C. The temperature is maintained until the alloy is melted and then the stack is allowed to cool.

FIGURE 2 is illustrative of the manner in which non-metallic refractory portions may be bonded to other non-metallic refractory portions in accordance with our invention. Such portions are bonded by inserting therebetween an alloy of nickel, titanium and an element selected from the group consisting of silicon and carbon. The bodies and the alloy are then held in contact and heated to a temperature range of 950° C. to 1200° C. until the alloy is melted and then allowed to cool.

The temperature range of 950° C. to 1200° C. at which the nickel–50 to 55 titanium–0.3 to 10 silicon or carbon alloy compositions are formed is below the melting point of any one of the metal members and the softening point of a large number of non-metallic refractories. Therefore, a very satisfactory bond is obtained without heating the metal members to a point at which the vapor pressure becomes appreciable and without heating the non-metallic refractory bodies to temperatures at which they soften. This is particularly desirable in the construction of vacuum tubes, since the contaminating or deforming effects which accompany the heating of tube parts very close to their melting temperature are avoided.

The non-metallic refractories used frequently in electron tube manufacture are tabulated in Table I which includes the temperature range at which they are formed. The formation temperature or softening temperature of a ceramic depends not only on the base material, but also on the type and variety of flux used. All of the below-mentioned ceramics are satisfactory for use in electron tubes since they have thermal coefficients of expansions sufficiently close to thermal coefficients of expansion of metals suitable for use in construction of electron tubes.

TABLE I

Ceramics

Class of Ceramic	Appl. Chem. Composition	Usual Maturing Temp. (Firing), °C.
Corundum	(Al_2O_3)	1,400–1,700
Forsterite	($2MgO\ .\ 1SIO_2$)	1,200–1,400
Steatite	($1MgO\ .\ 1SiO_2$)	1,200–1,300
Beryllia	(BeO)	1,400–1,800
Zircon (Talc)	ZrO_2SiO_2(MgO and Al_2O_3)	1,200–1,350

In FIGURE 3 of the drawing there is an application of our invention as it applies to the construction of a miniature triode. FIGURE 3 shows a triode consisting of an anode **1**, ceramic spacer **2**,, grid connecter **3**, grid **4**, ceramic spacer **5**, cathode assembly **6**, cathode connecter **7**, ceramic spacer **8**, and heater **9**. Members **1**, **3**, **4**, **7** and **9** as well as cathode **6** are made of titanium metal. Cathode **6** is electrically connected to cathode connecter **7** by means of a thin conductive film which formed on the lower side of ceramic spacer **5**. Ceramic members **2**, **5** and **8** are selected from a variety of ceramic having a thermal coefficient of expansion very nearly that of titanium. The tube is formed by stacking the members in the illustrated order with an alloy of nickel, 50 to 55 atomic percent titanium and 0.3 to 10 atomic percent of an element selected from the group consisting of silicon and carbon between the parts at the points marked **11**. The assembled tube parts and metal members are held together and placed in the chamber which is evacuated to a pressure less than 1 micron. The tube parts and metal members are then heated to a temperature exceeding 950° C. by conventional induction heating apparatus. After the tube structure reaches a temperature of above 950° C. the alloy is melted and hermetically seals the tube joints. The tube structure

is then allowed to cool in vacuum until the liquid alloy solidifies.

A tube formed in this fashion is very nearly completely free from contamination from evaporated metal. The bonding material which consists of nickel-titanium-silicon or nickel-titanium-carbon alloy has a thermal coefficient expansion which is nearly that of titanium and ceramic and is formed at a temperature below the softening point of the ceramic. Thus, there is formed a bond, all parts of which have approximately the same coefficient of expansion which is desirable in construction of tubes of the type illustrated in FIGURE 3 of the drawing.

Our invention is particularly advantageous in the construction of vacuum tubes. The metallic bond is comprised in part of a tough metallic layer which does not form to any significant extent in bonds formed utilizing only metals of the titanium, hafnium, zirconium and thorium group and those of the iron group. Therefore, the tendency toward weak spots and leaks is avoided. Since no gases are formed or liberated during sealing of a bond formed of metal members in accordance with our invention, it is not necessary to degas the tube.

The bond formed in accordance with the method of our invention may be obtained by heating the parts in any atmosphere which is relatively inert to titanium, nickel, iron or iron base metals. For example, the parts may be bonded in an atmosphere of argon, helium or in a vacuum. The heat may be applied in any suitable fashion.

While other modifications of this invention and variations thereof which may be employed within the scope of the invention have not been described, the invention is intended to include such that may be embraced within the following claims.

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

1. An article comprising a metal portion selected from the group consisting of nickel, titanium, iron and iron base metals, a non-metallic refractory portion, and an alloy of 50 to 55 atomic percent titanium, 0.3 to 10 atomic percent of an element selected from the group consisting of silicon and carbon, and the balance being nickel bonding said metal portion to said non-metallic refractory portion.

2. An article comprising non-metallic refractory portions, and an alloy of 50 to 55 atomic percent titanium, 0.3 to 10 atomic percent of an element selected from the group consisting of silicon and carbon, and the balance being nickel bonding said non-metallic refractory portions.

3. An article comprising a metal portion selected from the group consisting of nickel, titanium, iron and iron base metals, a hollow cylindrical non-metallic refractory portion, and an alloy of 50 to 55 atomic percent titanium, 0.3 to 10 atomic percent of an element selected from the group consisting of silicon and carbon, and the balance being nickel bonding said metal portion to said non-metallic refractory portion.

References Cited in the file of this patent

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2,962,136	Pineus	Nov. 29, 1960
3,031,737	Conley	May 1, 1963