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METHOD FOR TREATING WORKING AND BONDING REFRACTORY METALS AND ALLOYS

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ABSTRACT OF THE DISCLOSURE

A method of processing refractory metals and their alloys by cold working them while they are embedded in a TiNi matrix at a temperature above the recrystallization temperature of TiNi and below the recrystallization temperature of the refractory metal.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention pertains to refractory metals and their alloys and more particularly to novel means for processing these materials.

Refractory metal technology is a comparatively new field of metallurgy and although the existence of refractory metals and their properties have been known for a long time, their importance as engineering materials in high temperature and space technology has only recently been exploited. Consequently, in order to take advantage of the desirable inherent properties of these materials, there is a vast need for new methods for processing them; e.g., heretofore there was no satisfactory method for either cold working (defined in the Eighth Edition of ASM Metals Handbook as, "Permanent strain produced by an external force in a metal below its recrystallization temperature,") refractory metals or for forming articles such as tubing from them.

Accordingly, it is an object of this invention to provide novel means for processing refractory metals and their alloys.

It is another object to provide a novel method for working these materials.

It is a further object to provide a novel means for bonding these materials.

It is still another object to provide a novel means for protecting these alloys.

These and other objects will become readily apparent from reading the following detailed description of the invention.

The objects of this invention are accomplished by taking advantage of the unique compatibility that exists between nickel-titanium alloys comprising from about 53–62 wt./% nickel with the remainder essentially titanium (hereinafter referred to as TiNi), and refractory metals and their alloys (hereinafter the term "refractory metal" includes both refractory metals and refractory metal alloys). The TiNi based alloys are described in more detail in Patent No. 3,174,851 granted on Mar. 23, 1965, which is hereby incorporated by reference. As representative examples of the refractory metals that may be utilized in this invention, there may be mentioned: tungsten, rhenium, molybdenum, tungsten based alloys; such as, 3% rhenium remainder tungsten, 30–32% rhenium the remainder tungsten, 30% molybdenum the remainder tungsten, etc., the molybdenum based alloys; such as, 2% tungsten remainder molybdenum, 30% tungsten remainder molybdenum, etc., and the rhenium based alloys; such as, 47–50% molybdenum the remainder rhenium, etc.

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Accordingly, refractory metals may be effectively cold worked by working them while they are embedded in a TiNi matrix. More particularly, the refractory metal is embedded in a TiNi matrix (the TiNi preferably comprises from about 54–58 wt./% nickel with the remainder essentially titanium) by immersing the refractory metal in molten TiNi and allowing it to solidify in place. The resulting composite is then worked at a temperature above the recrystallization temperature of the TiNi and below the recrystallization temperature of the refractory metal, preferably between about 700° and 900° C., resulting in a cold working of the refractory metal and a hot working of the TiNi. The working may be effective by any one of a wide variety of well known working procedures including; for example, swaging, rolling, forging, extrusion, drawing, etc., and the starting configuration of the refractory metal may be of any size or shape including; for example, spheres, rods, strips, wires, etc. After the working is completed, the refractory metal is removed from the TiNi matrix by simply melting away the TiNi (tungsten melts at about 3410° C. and TiNi melts at about 1310° C.) in a controlled atmosphere. A slight coating of TiNi, probably in the form of oxides, may be left on the refractory metal to provide a protective coating as described hereafter or it may be removed by picking; e.g., using a solution of $8HNO_3:20H_2SO_4:8HF$.

The above procedure may be used for forming a wide variety of sizes and shapes of refractory metals; e.g., the above procedure may be utilized in forming refractory metal tubing. A hole is drilled in a refractory metal rod and it is then immersed in molten TiNi which is allowed to solidify. The resulting composite is then either swaged or extruded to the desired length and the TiNi is removed from both the internal bore and the outside of the tubing by melting in a controlled atmosphere. The resulting tubing may then be further treated by conventional processing procedures. It should be readily apparent from the above teachings that refractory metal tubing having a wide variety of desired dimensions may be easily produced, by properly selecting the dimensions of the starting material and the amount of work to be performed.

The above cold working technique is also extremely valuable for cold working refractory metals directly from the arc cast condition. Heretofore, due to the large equiaxial and columnar grain structure of the arc cast ingots, it was necessary to break down the cast structure by hot working; e.g., using extrusion techniques, before the ingot could be satisfactorily cold worked. Now, by cold working the arc cast refractory metal while embedded in a TiNi matrix it is possible to perform the "breaking down" and cold working fracture free, in a single step, by conventional working procedures; e.g., swaging, rolling, extrusion, forging, etc., without any previous hot working.

In utilizing the above teachings, it is to be understood that the known engineering and technological principles applicable to the working of metals, especially refractory metals, are equally applicable to the working process of this invention so long as the refractory metal is worked in a TiNi matrix and by utilizing these principles and the teachings of this invention those skilled in the art can readily manufacture refractory metal components having a wide variety of sizes, shapes and structural properties.

TiNi may also be utilized for bonding refractory metals by brazing techniques. TiNi (it preferably comprises 54–58 wt./% nickel, remainder essentially titanium) forms an excellent braze since it has the properties generally desirable for a brazing alloy; i.e., good wetting, a high melting point that may be even further increased after brazing, and a narrow diffusion zone that shows no evidence of brittleness under conditions of drastic plastic deformation. The TiNi brazing may be performed by any one of a wide variety of brazing techniques, particularly those applicable to refractory metals; e.g., a lap joint may be formed by melting and solidifying, in an inert atmosphere, a sheet of TiNi that has been placed between two partially overlapped pieces of a refractory metal. Since the techniques of brazing and preparing metals for brazing are well known in the art and these techniques are applicable to brazing refractory metals with TiNi, their details will not be set forth herein.

TiNi may also be used as a protective coating for refractory metals. Thus, it has been found that the coating of refractory metals with TiNi prevents the catastrophic oxidation that usually results when refractory metals are heated above a certain temperature in air. Morever, the TiNi provides a tight protective coating which reduces notch sensitivity and increases resistance to chemical and corrosive action. It has also been found that the mechanical properties of the coated refractory metal are influenced by the TiNi alloy composition; e.g., a TiNi alloy with good hardness properties (60 wt./% nickel the remainder essentially titanium) increases abrasion resistance, and thus it should be readily apparent that the effect of the TiNi on the mechanical properties of the coated refractory metal will be considered in selecting the particular alloy composition.

The refractory metal may be coated with TiNi by any one of a wide variety of coating procedures; e.g., by dipping the refractory metal in molten TiNi and allowing the TiNi coating to solidify on the metal. Since these coating procedures are well known in the art and such procedures may be employed for coating refractory metals with TiNi, their details will not be set forth herein.

The following examples are illustrative of the invention but they are not to be considered as limiting it in any manner.

EXAMPLE I

Several arc cast tungsten balls that had not previously been treated, each having ⅛" diameter, were placed in a mold and TiNi (55.1 wt./% nickel, the remainder essentially titanium) was melted around it. The TiNi was allowed to solidify and the TiNi matrix having the tungsten balls embedded in it was swaged at 900° C. The tungsten balls elongated fracture free to a 1/16" diameter. The tungsten also showed no signs of oxide vaporization indicating that the TiNi acted as a protective coating.

EXAMPLE II

Three tungsten rods having diameters of 0.0935", 0.146" and .250", respectively, were placed one on top of the other in a graphite mold so that they were concentric about an axis through their centers and TiNi (55.4 wt./% nickel remainder essentially titanium) was melted around them. The TiNi was allowed to solidify and the TiNi matrix having the tungsten embedded in it was swaged at 900° C. until the diameters of the rods were 0.047", 0.073" and 0.125", respectively. The rods diameters were reduced in equal proportions without fracture.

EXAMPLE III

Tungsten tubing was made by the following procedure. A 3/16" diameter bore was drilled in a tungsten rod having a ½" diameter. The rod was placed in a graphite mold and TiNi (55.4 wt./% nickel, the remainder essentially titanium) was melted around it. The TiNi was allowed to solidify and the resulting matrix having the tungsten rod embedded in it was swaged at 900° C. until the tungsten rod had an outside diameter of .150" and an inside bore of 1/16". The matrix containing the tungsten tube was placed in a furnace and the TiNi was melted out. The remaining TiNi coating in the form of an oxide was removed by pickling, using a solution comprising,

$$8HNO_3:20H_2SO_4:8HF$$

The finished piece of tungsten tubing showed no signs of fracture.

EXAMPLE IV

Two strips of tungsten (2.5" x ½" x .02") were joined together using a ¼" overlap joint and a TiNi braze (56.5 wt./% nickel, the remainder essentially titanium).

The tungsten strips were overlapped and a ¼" x ½" x .009" piece of TiNi sheet was placed between them. The bars with the TiNi between them were placed in the hot portion of a tube furnace having an argon atmosphere and heated to a temperature ranging from about 1,310° C. to about 1,360° C., to melt the TiNi. The strips were cooled to about 1,250° C., to solidify the TiNi, removed from the furnace, and allowed to cool to room temperature. The resulting braze had good weting and a strong bond was formed.

EXAMPLE V

The above procedure was used to bond together two 3" x ½" x .02" molybdenum strips. Once again the resulting braze had good wetting and a strong bond.

This invention provides an effective means for processing; i.e., working, bonding and protecting, refractory metals which will considerably widen their field of use. By effectively using the teachings of this invention those skilled in the art will be able to take full advantage of the desirable inherent properties of these materials.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A process for cold working a refractory metal, said refractory metal being selected from the group consisting of tungsten, rhenium, molybdenum, alloys of tungsten and molybdenum, alloys of tungsten and rhenium and alloys of molybdenum and rhenium, said process comprising: working the refractory metal while it is embedded in a nickel-titanium alloy matrix, said working being effected at a temperature below the recrystallization temperature of the refractory metal, said nickel-titanium alloy comprising 53–62 wt./% nickel, with the remainder being essentially titanium.

2. The process of claim **1** wherein said nickel-titanium alloy comprises from about 54–58 wt./% nickel with the remainder essentially titanium.

3. The process of claim **1** wherein said refractory metal is in arc cast condition.

4. The process of claim **1** wherein the refractory metal's arc cast structure had been broken down previous to working.

5. The process of claim **2** wherein said refractory metal is tungsten.

6. The process of claim **2** wherein said refractory metal is molybdenum.

7. The process of claim **2** wherein the working temperature is between about 700° C. and 900° C.

8. The process of claim **1** wherein the refractory metal is in the form of a rod having a bore in it and the working is performed by swaging.

9. The process of claim **1** wherein the refractory metal is in the form of a rod having a bore in it and the working is performed by extruding.

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