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2,805,148

METHOD OF MELTING REFRACTORY METALS

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No Drawing. Application October 21, 1952,
Serial No. 316,093

7 Claims. (Cl. 75—84)

This invention pertains to an improved method for deforming solid refractory metals such as titanium, zirconium and the like. In a particular application it pertains to the perforation or tapping of special metallurgical furnaces used for the preparation of these refractory metals and their alloys.

It is well known that titanium metal is of commercial importance and that great effort is being made to produce it in large quantity. Certain characteristics of the metal give rise to new problems in its metallurgy, fabrication and handling. For example the high melting point and great chemical affinity of titanium for oxygen and nitrogen make it practically impossible to melt titanium in contact with air or any of the known refractories without serious contamination. Even when cutting solid titanium with the conventional oxygen torch the absorption of oxygen into the metal at the heated point is sufficient to impart unwanted properties at least to the surface of the work. In welding, the use of oxygen is entirely unsatisfactory due to formation of oxide so it has become necessary to use arc welding technique under a protective helium atmosphere.

The metallurgy of titanium and like refractory metals has been greatly hampered by the fact that the pure metal cannot be contained in known solid refractories without contamination. Graphite and water-cooled copper have been used as melting containers respectively in induction melting and arc melting processes. Only in the graphite containers can any appreciable quantity of liquid exist and that is quickly contaminated with as much as 0.5% or more of carbon. One unique refractory may be used with molten titanium and that is solid titanium itself. It has therefore been proposed that furnaces and crucibles for containing molten titanium and similar metals be lined with a layer of the metal itself and maintained "frozen" as a solid shell by external cooling. Such furnaces must therefore be heated from the top as by radiation from a refractory roof and electrical heaters. The depth to which a metal may be melted by this means is quite limited and the fabrication of a valve for controlling the withdrawal of the melt into ingot molds is virtually impossible. At the expense of complicated and heavy construction the furnace can be tilted to pour out the contents, but even here the formation of a pouring spout or lip is a problem. Such problems are amplified by the fact that these metals must be melted under a protective atmosphere of an inert gas such as argon.

In the steel industry the melt is withdrawn from refractory containers by a process known as tapping. The ceramic refractory is broken out at the tap hole and the solid steel closing this outlet is burned through with an oxygen torch or "lance" thus releasing the molten metal charge. This oxygen flame is not suited for use with titanium due to the detrimental effect of even traces of oxygen.

It is an object of this invention to provide a non-contaminating means for deforming, especially perforat-

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ing, solid refractory metals such as titanium and zirconium and their alloys. A more specific object is to provide an improved means of tapping crucibles and furnaces in which the molten refractory metal charge is separated from the furnace walls by a solidified layer or shell of the same refractory metal. Such a protective layer of the solidified metal is hereinafter called a "skull" and the furnace involved a "skull furnace." A further object is to provide means of deepening the molten metal pool, of decreasing the thickness of the skull, and of altering the shape of the metal pool in a skull furnace.

The above and other objects are achieved by this invention which comprises deforming a solid refractory metal composition by locally contacting the body of said composition with elemental chlorine, initiating chemical reaction between the two, and maintaining said reaction until a portion of the solid phase of said body is transformed to another physical state.

A specific embodiment comprises locally contacting a refractory metal furnace skull, which is restraining or containing the molten metal phase, with a stream of chlorine gas at a point below the level of the contained molten metal, initiating reaction between said chlorine and the metal skull and continuing the reaction until, by virtue of chemical erosion and melting, a hole is forced through the solid metal skull and the contained molten metal is free to exhaust through the opening.

In a more specific embodiment the chlorine stream or jet is applied to a skull consisting of a major portion of at least one of the metals selected from the group comprising titanium, zirconium and hafnium, said chlorine being directed from a nozzle of water-cooled metal, initiating and maintaining reaction between the chlorine and the metal of the skull until tapping of the furnace charge is effected.

In a further modification the nozzle may be made of graphite in which case it is possible to plunge it, with the chlorine on, into the furnace melt and contact the skull from the interior. By this means the skull may be reduced in thickness or even tapped from inside.

This novel tapping method may be illustrated by the following example: A 10 x 10 inch graphite crucible was filled with titanium sponge and heated in an induction furnace in a protective argon atmosphere. As the metal melted more was added to fill the crucible. The charge was allowed to cool until a portion of the metal solidified. The liquid charge was then poured out leaving a skull roughly two inches thick lining the crucible. When cold, a small tap-hole was drilled in the side of the graphite crucible near the bottom but not through the titanium skull. This lined crucible was then set up in the induction furnace but further heat was made available from an arc electrode of water-cooled tungsten located centrally above the crucible. A cold graphite ingot mold was placed under the tap hole. When the crucible was charged with titanium sponge and protected with argon the arc was struck against the sponge and a central pool of molten metal formed. The crucible itself was heated mildly by induction when needed but was kept below the titanium melting point of 1725° C. Thus the protective skull prevented carbon contamination of the second batch of metal. When the pool had formed, a jet of chlorine from a carbon tube was impinged on the skull through the crucible tap hole. A violent reaction occurred at this spot and as a result the skull was perforated. Although the lower part of the skull had increased in thickness due to heat losses, the chlorine opened the passage. When the ingot mold was full, as judged by its increased weight, the tap-hole was stopped by pressing the apex of a thin water-cooled copper cone against the hole. The titanium froze at once and the copper cone was easily retracted from the crucible. Further melting of metal by arc heat-

ing and tapping with chlorine could follow in a cyclical manner. Analyses of this ingot showed less than 0.1% carbon while the metal poured from the first straight induction heating contained over 0.6% carbon.

The chlorine used in this invention may be the usual commercial compressed gas but it is preferable to have it substantially free of hydrogen, oxygen and nitrogen. Dilution with inert gases such as argon may be practiced to moderate the violence of the reaction but undiluted chlorine is preferred in most cases.

The refractory metals to which this technique is applicable with advantage are those found in the A sub-groups of groups IV, V and VI of the periodic table, namely titanium, zirconium, hafnium, vanadium, columbium (niobium), tantalum, chromium, molybdenum and tungsten. Greatest advantage is shown in the titanium sub-group due to the extreme sensitivity to oxygen, nitrogen, etc. The high melting alloys especially those containing fifty or more weight percent of the foregoing refractory metals may also be handled by this method since they likewise have this great affinity for oxygen, nitrogen and other elements which are held interstitially in the metal.

In many cases the reaction between the metal and the stream of chlorine is self starting, i. e. the metal to be deformed or punctured is often at temperatures high enough to start the formation of the metal chloride. If the reaction is not spontaneous the surface of the metal may be heated by striking an electric arc. This is preferably done in an inert atmosphere (absence of air) or in the chlorine atmosphere of the jet. Conveniently, the chlorine jet may be the arcing electrode which may be made of cooled metals such as copper, titanium, silver, or even the low boiling metals such as magnesium, and zinc. The cooling may be done with water jackets or by other cooling fluids. Cooling prevents destruction of the jet by the chlorine or its melting when close to the heated zone. Graphite may be used without cooling, and, due to the relatively small mass of it in contact with the charge, the contamination is practically negligible.

Since the pouring and handling of these heated refractory metals is preferably done out of contact with air and moisture in order to maintain purity, a suitable hood or enclosure filled with argon may be used during the operation. This device may simultaneously serve to carry off the volatile metal chlorides produced.

A "skull" furnace heated by radiation from above the charge is found to carry a rather shallow pool of molten metal. For various reasons particularly related to uniformity of product and the pouring of large ingots, it is desirable to increase the depth of this pool. According to my discovery the pool depth can be rapidly increased by sparging the pool with chlorine. This may be accomplished by forcing chlorine through a graphite pipe inserted from the top of the furnace. The tip of the nozzle may be brought near the solid metal "skull" to obtain melting at the desired location e. g. where the skull is thickest. As a result of the heat of reaction between the chlorine and the refractory metal the pool may be deepened. The jet of chlorine may then be held at the tap hole location and the furnace "tapped" by opening the tap hole from the inside. In a practical application the skull furnace may be loaded with titanium from a metallurgical step or from a melting operation. Due to heat losses through the skull the metal appears as a solid at the bottom leaving only a shallow pool. This pool may be deepened by the procedure just outlined or the original melt may be maintained in the molten state by sparging with chlorine. Alternatively the sparger nozzle may be located in the bottom of the furnace so that the metal is maintained in a molten state down to a level near this chlorine inlet. Obviously, a multiplicity of spargers or jets may be used to operate simultaneously if desired and to widen the lower portion of the liquid body.

In both sparging methods it is feasible to make a supply of argon or other inert gas, e. g. helium, available to the nozzle so that its passage may be maintained open after the metal has reached the desired temperature and the chlorine is turned off. For control of this highly exothermic reaction the argon may be mixed with the chlorine to moderate the reaction temperature. In this way a minimum of chlorine may be used in conjunction with good agitation of the melt.

Chlorine is probably unique in this use since it reacts readily with most refractory metals, especially titanium, at slightly elevated temperatures, but unlike oxygen, does not contaminate the metals. The only products formed at the high temperatures involved are volatile and escape. When chlorine is in excess, $TiCl_4$ is probably the product. With less chlorine the lower chlorides such as $TiCl_2$ may form but these too are volatile at the temperature of the molten metal. In the case of some alloys the lower chlorides may remain on the solid surface but they do not tend to penetrate deleteriously as oxides would.

In most cases it is believed that this method of deforming metal operates by both chemical consumption of the metal and by melting. The reaction between chlorine and titanium for example is highly exothermic and the released heat is sufficient to melt some of the solid metal in the vicinity of the reaction. This is particularly true in furnace tapping where at least portions of the skull are already very hot. On the other hand when cutting cold metal the chlorination reaction may proceed at temperatures far below the melting point and due to rapid heat losses from the cutting zone, no actual melting of the metal, or at least a very little, will be observed. When operating in a protective atmosphere of an inert gas or argon at above about $1100^\circ C$, the work is exceptionally clean because, unlike oxy-cutting products, all combustion products are volatile. However, it is possible to rig enclosures and mechanically operated jets so that the air and moisture may be excluded by an atmosphere of $TiCl_4$. After the work is cooled in this atmosphere the resulting scale of lower chlorides may be removed by annealing in argon or it may be dissolved or mechanically cleaned off.

The torch as a whole or the nozzle may be designed to alter the stream of chlorine to suit the type of cutting or welding desired. Thus, it may be of high or low velocity and thick or pin-pointed. It is further possible in lieu of a protective enclosure, to connect the torch to both chlorine and a source of an inert rare gas such as argon. When the chlorine burning step is finished the torch is quickly switched to the inert gas and the work cooled under its protective blast.

This invention has the advantage over prior art methods that it furnishes non-contaminating means of melting, deforming, cutting, and even welding of refractory metals which are very sensitive toward oxygen.

A particularly interesting advantage of this method lies in its ability to replace wholly or in part the conventional heating elements in a "skull" furnace. In general, such melting furnaces may be greatly simplified by the methods herein described, thus, the cumbersome operations of pouring by tilting, agitation by rocking, and heating by downward radiation may be eliminated by chlorine sparging and tapping.

I claim:

1. A process for deforming a contour of a solid titanium metal skull retaining molten titanium within a heat-treating vessel to remove the molten titanium therefrom which comprises directing a stream of chlorine against a surface of said skull while the latter is at its reaction temperature with chlorine, reacting said chlorine with said titanium skull until melting a portion of said skull occurs and the deformation desired in the contour and perforation of said skull becomes effected, and withdrawing said molten titanium from said vessel through said perforation.

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2. A process for perforating a solid titanium skull protective liner employed within a heating vessel to withdraw a pool of molten titanium retained in said skull within said vessel which comprises directing a stream of chlorine into said pool of titanium for reaction with said skull, continuing said chlorine introduction until a portion of said skull becomes melted and perforated, and withdrawing said molten titanium from said vessel through the perforated portion of said skull.

3. A process for removing a molten metal product selected from the group consisting of titanium, zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum and tungsten, from a heating and melting zone wherein said product is retained on a protective body of the same metal in solid state, comprising melting and perforating a portion of said solid protective body while at its reaction temperature with chlorine by directly applying a stream of chlorine thereagainst, and withdrawing the molten metal product from said zone through the resulting perforation in said protective body.

4. A process for removing molten titanium from a heating and melting zone wherein said titanium is retained on a solid titanium protective body, comprising melting and perforating a portion of said solid titanium body while the latter is at its reaction temperature with chlorine by directly applying a stream of chlorine thereagainst, and subsequently withdrawing the molten titanium from said zone through the perforation formed in said solid titanium body.

5. A process for withdrawing molten titanium from a heating and melting vessel wherein said molten titanium is contained within a solid titanium protective body which comprises striking an arc against said body until its temperature locally is the least equal to the initial reaction temperature of titanium with chlorine, applying a stream of chlorine against the locally heated area of said body until a perforation occurs therein, and removing said molten titanium from said vessel through the perforation thus formed.

6. A process for tapping and removing molten titanium from a solid titanium vessel in which it is contained, comprising striking an arc between said vessel and a hollow electrode to locally heat said vessel to at least the reaction temperature between titanium and chlorine, directing a

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stream of chlorine through said electrode against the heated surface at the location of said arc, allowing the chemical action of the chlorine with the heated titanium to puncture said titanium vessel, and removing the molten titanium content of said vessel through the perforation resulting from said puncture.

7. A process for removing molten titanium metal from a skull furnace in which said titanium in the form of a pool is supported by a solid skull of titanium, comprising puncturing said solid titanium skull support below the surface of the molten titanium pool by locally heating said skull to above the reaction temperature of titanium with chlorine, impinging a stream of chlorine on the site of said local heating until said support becomes punctured, and withdrawing the molten titanium from said skull in molten condition through the skull puncture thus formed.

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