

Sept. 5, 1967

G. L. DURFEE ETAL

3,339,271

METHOD OF HOT WORKING TITANIUM AND TITANIUM BASE ALLOYS

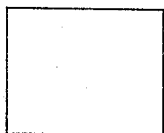
Filed July 1, 1964



UNSHAPED BLANK OF TITANIUM OR TITANIUM BASE ALLOY.



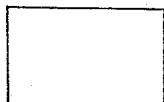
CONVENTIONAL CLEANING, AND MILD ACID ETCHING OF UNSHAPED BLANK'S SURFACES, TO PREPARE SAME FOR ELECTROLESS NICKEL-PLATING.



IMMERSION OF SO-PREPARED UNSHAPED ^{BLANK} IN CONVENTIONAL AQUEOUS ELECTROLESS NICKEL-PLATING SOLUTION, LONG ENOUGH FOR CHEMICAL DEPOSITION ON BLANK SURFACES OF A UNIFORM NICKEL-PHOSPHORUS PLATING OF A THICKNESS IN THE RANGE OF 0.2 MIL TO 2 MILS.



PROLONGED HEATING IN FURNACE OF SO-PLATED UNSHAPED BLANK, UP TO AN ELEVATED TEMPERATURE IN THE RANGE OF 1600° TO 1850°F



HOT WORKING OF SO-PLATED AND SO-HEATED UNSHAPED BLANK, BY FORGING DIES OR EXTRUSION DIES, TO DESIRED OR PREDETERMINED SHAPE.

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1

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3,339,271

METHOD OF HOT WORKING TITANIUM AND TITANIUM BASE ALLOYS

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Filed July 1, 1964, Ser. No. 379,728
2 Claims. (Cl. 29—528)

Our invention resides in an improved method or process for the hot working, by forging or the like, of titanium and titanium base alloys.

These high-cost metals, by virtue of being light yet very strong, as well as remarkably able to withstand very high service temperatures, are extremely important materials in the aircraft industry and also in the aerospace industry. Throughout both of these key industries, there are great numbers of various critical parts and components, of all sizes and shapes, which for strength and weight-saving purposes, and/or for high temperature service purposes, must needs be provided by high quality forgings of titanium and titanium base alloys.

These metals, however, are difficult to forge, being much less amenable to standard forging procedures than are various other industrial metals, both ferrous and non-ferrous. Consequently, it has not heretofore been possible, except at great trouble and expense, and much wasteful machining away of these high price materials, to produce titanium and titanium alloy forgings which possess in full measure the optimum properties of soundness, wroughtness and close dimensional accuracy, that are more and more being demanded for great numbers of the titanium and titanium alloy forgings which go into the products of these two industries.

Our invention, as hereinafter described, provides certain novel and inexpensive protective measures which so effectively enhance the forgeability of titanium and titanium base alloys, that precision-forged parts or components of these metals, fully meeting the exacting demands of these two industries for utmost quality and dimensional accuracy, can readily be produced by standard forging procedures. Our invention thus makes an important contribution to aeronautical and aerospace progress.

Our invention is described herein with specific reference to the forging of titanium and titanium base alloys. However, our invention is equally applicable and useful when titanium and titanium base alloys are subjected to other hot working operations, such as extrusion, hot rolling, heat treating and the like, where the same need exists as in forging, to protect the unshaped titanium metal, throughout its prolonged exposure to the high temperatures required for such hot working, from any access thereto of furnace gases and/or atmospheric gases.

The need for this protection stems from the fact that titanium metal, at these high temperatures, is extremely vulnerable to attack, and to contamination in depth, not only from the oxygen and nitrogen of the air, but also from hydrogen, which is a common constituent of furnace gases. Thus it is that unprotected or poorly protected forging blanks of titanium and titanium base alloys, from their prolonged sojourn in the usual heating furnace, will often be damaged by severe hydrogen embrittlement. Furthermore, at these extremely high temperatures, titanium metal is very susceptible to sub-surface penetration and contamination by oxygen and nitrogen, both of which form with the penetrated hot metal various stable compounds and solid solutions, all of hard and very refractory nature.

It is the presence on heated titanium forging blanks of these thick contaminated outer portions which makes said blanks so very difficult to forge in an accurate and satis-

factory fashion. The extreme hardness of these badly contaminated outer portions causes rapid and costly wear and scarification of the forging dies, by which said heated blanks are shaped and worked. Furthermore, the action of these forging dies on these hard, non-ductile outer portions results in titanium and titanium alloy forgings whose exterior surfaces are severely and unevenly cracked and fissured. Thus it has been the practice to use oversize forging blanks of these costly metals, and to forge same to dimensions considerably in excess of those contemplated for the finished forgings, in order to give leeway for complete removal, by machining, of these thick, contaminated, severely cracked outer portions of the forged titanium parts. Since this machining must be performed in depth on extremely hard and severely cracked material, it involves rapid and excessive tool wear, which is still another factor that greatly increases the cost of acceptable forgings of titanium and titanium base alloys.

Previous attempts to protect titanium forging stock, throughout its heating and forging cycles, against the above-described deep-seated and costly contamination by ambient gases, have involved pre-coating of said stock, either with ceramic materials, or with various more ductile metals. One such proposal in the last category, is that of Hanink et al. Patent No. 2,903,785, titled Method of Hot Working Titanium. As taught by this patent, the unshaped titanium or titanium base alloy forging stock, by a hot dipping process initially receives a thin coating of molten aluminum. This thin aluminum coating is allowed to cool and harden on the forging stock before the latter by prolonged sojourn in the usual furnace is gradually brought up to the high temperature range (1600°–1850° F.) required for the forging of titanium and titanium base alloys. However, the fact that aluminum has a melting point (1220° F.) which is well below this forging temperature range for titanium, makes it probable that considerable portions of this thin aluminum coating, quickly made molten by the high temperatures within the furnace, would just as quickly run off, uselessly, from the titanium forging stock. In any event, even if some of molten aluminum tends to alloy, as asserted in this Hanink et al. patent, with the titanium surfaces, it seems fairly obvious that all such titanium-aluminum surface portions, due to the very high temperature of their titanium content, will be as badly attacked and as deeply contaminated by ambient gases as are the surface portions of unprotected titanium forging stock.

Nickel, as a relatively ductile and readily-applied coating or plating metal, has a melting point (2651° F.) much higher than aluminum, and also well above the high temperature range which must be reached for the forging of titanium and titanium base alloys. But in spite of this manifest advantage possessed by nickel (by comparison with aluminum) as a ductile protective coating for titanium forging stock, it appears that, up to now, various previous attempts to employ nickel for this purpose have consistently met with failure. As stated in column 1 of Milnes Patent No. 2,900,715, titled Protection of Titanium:

“... it has been proposed to protect forging blanks of titanium from these effects by enclosing them in electrodeposited envelopes of nickel. This proposal, however, has not met with success, apparently for the reason that nickel—at least in layers that are thin enough to flow with the underlying metal during forging operations—is not impervious to hydrogen and possibly is not impervious to other gases that are ordinarily found in heating furnaces of the types ordinarily employed, or in air.”

It has also been observed that thin platings or coatings of electrodeposited nickel on titanium forging stock have

a pronounced tendency to fracture and peel off from the titanium base metal, whilst the latter is being heated up to forging temperature. It appears likely that this may be due, in part at least, to the release by this intense heating of certain residual stresses that are set up or created in the nickel plating by the conventional electroplating process.

However that may be, we have discovered unexpectedly that nickel can be made to serve effectively in ideal fashion, as a durable, ductile and impenetrable thin protective coating for titanium forging stock provided always that said nickel, in lieu of being deposited on the titanium or titanium base alloy forging stock by conventional electroplating procedures, is instead deposited catalytically on each unshaped blank or slug of such stock by chemical reduction in aqueous solution, i.e., by the plating process popularly known as "electroless nickel plating."

This electroless or chemical nickel plating, both by the simple "batch method" described in Brenner et al. Patent No. 2,532,283, and by the more complex "continuous method" of Talmey et al. Patent No. 2,658,839, is being utilized commercially in various situations wherein already finished and shaped metal parts stand in need for service purposes, of special and long-lasting protection against corrosion, or where surfaces of such finished metal parts need to be given higher resistance to wear and abrasion. For example, it has been proposed, by Lee et al. Patent No. 2,928,757, to nickel plate, chemically or electrolessly, the surfaces of already finished and shaped articles of titanium and titanium base alloys, by way of overcoming the objectionable galling and high frictional characteristics of such titanium surfaces. However, to the best of our knowledge and belief, this electroless nickel plating has never before been employed, as contemplated by our invention, for creating upon unshaped blanks or slugs of titanium and titanium base alloy, before the usual prolonged heating of same required for their forging or other hot working, of thin ductile nickel-phosphorus platings or coatings, for service during such heating and subsequent hot working of the unshaped stock, as durable and effective barriers against any access, to the heated titanium metal, of furnace gases and of atmospheric gases.

In the practice of our invention as shown schematically by the accompanying flow chart, each unshaped blank or slug of, titanium or titanium base alloy forging stock is prepared for either "batch" or "continuous" electroless nickel plating by conventional procedures that are well known in the plating art. For example, an initial cleaning of the unshaped forging stock by sand blasting or shot blasting, may be followed if deemed necessary, by brief immersion of said stock in any suitable liquid alkaline cleaning solution. Then, after rinsing in cold water, the so-cleaned titanium forging stock, for activation of its surfaces, is immersed briefly in any suitable mild acid etching or pickling solution. For this purpose, we have employed very successfully an acid etching solution consisting approximately of 25% nitric acid, 2½% hydrofluoric acid, and the balance water. Then, after another rinse in cold water, the titanium or titanium base alloy forging stock is ready for prolonged submergence in any of various chemical nickel plating baths that are commercially available for the practice, either batchwise or continuously, of this electroless or chemical nickel plating.

These chemical plating baths, as fully described in the aforesaid Brenner et al., Talmey et al., and Lee et al. patents, are aqueous solutions, which contain, along with other ingredients, appreciable quantities of nickel salts and alkaline hypophosphites. As is well known, submergence in such aqueous solutions of various metals (including titanium and titanium base alloys) obtains, by catalytic deposition and chemical reduction, a slow but very uniform coating or plating of the submerged metallic bodies with nickel, alloyed with a small amount (from 5% to 15%) of phosphorus. A chemical nickel plating bath solution which we have used very successfully for

this electroless nickel plating of unshaped titanium and titanium base alloy stock to prepare same for forging, or for other hot working such as hot extrusion, is a commercial preparation which is supplied under the trade name "Enplate 410" by Enthone, Inc., of New Haven, Conn. It is obvious, however, that many other similar chemical plating bath solutions, could as well be employed. This is clear, not only from numerous patents which have been issued on such chemical plating baths, but also from a comprehensive treatise, "Symposium on Electroless Nickel Plating," published in 1959 by American Society for Testing Materials, of Philadelphia, Pa.

In this chemical or electroless nickel plating, the continuous method (of the aforesaid Talmey et al. patent) obtains deposition of the nickel-phosphorus plating at a considerably faster rate than is obtainable with the simpler batch method. Also, as is well known, the rate of nickel-phosphorus deposition, under both of these methods, can be measurably increased by maintaining the chemical plating bath at a temperature slightly below its boiling point. Our invention is in no way concerned with the rate at which the nickel-phosphorus coating is deposited or built up on the unshaped titanium or titanium base alloy stock which is destined for forging or other hot working operations. Our concern rather is with said coating's thickness, which depends upon the length of time that the titanium or titanium base alloy stock, cleaned and prepared as above described for electroless nickel plating, is allowed to remain submerged in any selected chemical plating bath. We have found that the purposes of our invention are best served by giving to the titanium or titanium alloy blanks or stock, nickel-phosphorus coatings which have a thickness ranging between two-tenths of a mil and two mils. Nickel-phosphorus platings of the extreme thinness represented by the lower portions of this range are adequate for titanium or titanium alloy forging blanks whereon the subsequent forging and shaping operations produce relatively small areal increases in the surfaces covered by said platings. The somewhat thicker nickel-phosphorus platings represented by the upper portions of this range are suitable for titanium or titanium base alloy forging or extrusion blanks, whereon the subsequent forging or extruding operations produce considerable areal increases in the surfaces covered by said platings.

When so-plated titanium or titanium base alloy blanks are introduced to and kept in a heating furnace, to bring them into the temperature range (1600°-1850° F.) required for their forging or extrusion, they suffer no hydrogen embrittlement from the furnace gases. This is because their protective nickel-phosphorus coatings, although very thin, are much more dense and far less porous than the thin platings of electrodeposited nickel which have heretofore been tried and found wanting for the protection of heated titanium. Nor are these chemically-deposited nickel-phosphorus platings on the titanium or titanium base alloy stock ever adversely affected (as are electrodeposited nickel platings) by the intense heat encountered in the furnace. On the contrary, this intense heating has a very favorable effect on these nickel-phosphorus platings, in that said heating, though not sufficient to melt said platings, does cause them to become very strongly diffusion bonded to the underlying titanium or titanium alloy stock.

This diffusion bonding serves to integrate the thin nickel-phosphorus coating or plating with said titanium or titanium base alloy forging stock, so that said plating remains intact and always flows uniformly with the heated titanium metal, during subsequent hot working and shaping thereof either by forging dies or by extrusion dies. In short, such thin nickel-phosphorus coatings on unshaped titanium or titanium base alloy stock have their protective capabilities enhanced, by the heating which said stock must undergo, before it can be forged, extruded, or otherwise subjected to working and shaping.

5

And since these protective nickel-phosphorus coatings are not broken or impaired, but only thinned out somewhat, by the action on said heated stock of forging dies or of extrusion dies, said coatings serve effectively and constantly to envelop the heated titanium metal to prevent any contamination thereof, either by furnace gases and/or by the gases of the atmosphere. Furthermore, these diffusion bonded nickel-phosphorus coatings are of so much inherent lubricity, that wear of the forging dies or of the extrusion dies, from their frictional contact with and pressure against said coatings is reduced to a minimum, also, this lubricity of their thin nickel-phosphorus coatings enables unshaped forging blanks and extrusion blanks of titanium and titanium base alloys to be effectively worked and shaped, by forging dies and extrusion dies respectively, with much less expenditure of power than would be required for the equivalent working and shaping of uncoated blanks of these metals.

We claim:

1. In the hot working of titanium and titanium base alloys, wherein unshaped blanks of such metals are subjected to prolonged heating in a furnace, to an elevated temperature in the range of 1600° to 1850° F., before being hot worked to a desired or predetermined shape, the improvement which consists in depositing electrolessly and catalytically on each unshaped blank, prior to its

6

said heating, a thin nickel-phosphorus plating by chemical reduction in an aqueous solution wherein each unshaped unheated blank is temporarily submerged, the plating being diffusion bonded to said blank by said heating.

2. The improved method of hot working titanium and titanium base alloys as claimed in claim 1, wherein each unshaped blank's submergence in said aqueous solution is of sufficient duration to deposit thereon a nickel-phosphorus plating having an initial thickness ranging between two-tenths of a mil to two mils.

References Cited

UNITED STATES PATENTS

15	1,345,441	7/1920	Hisamoto	72—46 X
	2,653,494	9/1953	Creutz	72—46 X
	2,900,715	8/1959	Milnes	72—47 X
	2,992,135	7/1961	Finlay	72—47 X
	3,040,426	6/1962	Hamren	29—528 X
20	3,080,643	3/1963	Hanink et al.	29—528
	3,147,547	9/1964	Kugbrich et al.	29—528
	3,154,849	11/1964	Dolch	72—46

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