

## UNITED STATES PATENT OFFICE

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PROCESS FOR HEAT-TREATING TITANIUM  
IN A FUSED BATH

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This invention relates to the processing of titanium and its alloys, and contemplates treatment by means of a salt composition adapted to form on titanium and its alloys a thin adherent protective surface coating. The molten salt may be used as an annealing bath, a rolling lubricant, or otherwise.

This application is a continuation-in-part of abandoned application Serial No. 114,452, filed September 7, 1949, by the same applicants.

By reason of the extraordinary chemical reactivity of titanium, particularly at elevated temperatures, it becomes difficult to maintain the metal and its alloys at a temperature and for a time which effect adequate annealing. Atmospheric oxygen and nitrogen are both readily absorbed in the surface metal at relatively low temperatures, and at higher temperatures these absorbed gases diffuse into the interior, materially altering tensile properties and hardness. Annealing in a vacuum, or in an atmosphere of an inert gas, such as argon, is troublesome and not entirely satisfactory, due to the almost inevitable presence of fractions of reactive gases in the closed annealing chamber. The common salt baths at the usual working temperature readily attack and destroy titanium.

The present invention comprises the discovery that the presence of an adequate amount of lithium in a conventional salt bath, say one comprising a halogen salt of an alkali metal, and an oxidizing salt, produces a thin adherent surface film which completely protects the metal from attack. Such a salt bath as one comprising equal parts of potassium chloride and sodium carbonate very readily attacks titanium. However, if about 6% of a lithium compound, such as lithium chloride, is added to this bath, a protective film is formed, which enables the annealing of titanium and its alloys at temperatures at least as high as 1600° F. Moreover, the bath may be held at 1600° F. for several hours, and at a temperature of 1200° F. for a period of days, without appreciable loss of lithium or other undesired effect. Working temperatures, up to about 1600° F., are determined by the results desired. The characteristic of this salt composition is its ability to form a titanate, e. g., lithium titanate, at working temperature, and to accomplish this purpose it has been found that the bath must contain lithium, an oxidizing radical, and a halide, other than a fluoride, of an alkali metal.

The present invention comprises not only the discovery of the passivating effect of lithium in

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molten salt baths which otherwise attack titanium, but further discovery that lithium is retained in such baths at temperatures up to at least 1600° F. Prior uses of lithium salts in salt baths have been merely as an alternate for another alkali metal salt, in baths which under operating conditions did not attack the metal under treatment even with no lithium present; or as a means of lowering the melting point of the salt mixture to enable its use at lower temperatures. The working temperatures of 1200° F. to 1600° F. contemplated under this invention are some hundreds of degrees higher than hitherto proposed for baths containing lithium, and the baths of this invention are the only ones known which do not attack titanium and its alloys at temperatures at which titanium can be annealed.

A preferred bath comprises about 47% potassium chloride, about 47% of sodium carbonate, and about 6% lithium chloride. This formula, however, is subject to wide variation.

As above set forth, the essential ingredients have been found to be lithium, an oxidizer, and a halogen salt of an alkali metal. Present in the bath are ions of lithium, ions of one or more of the alkali metals, and ions of a halogen other than fluorine. The lithium may be introduced as a metal, or it may be derived from one or more of a wide variety of lithium salts including the fluoride, carbonate, phosphate and bromide, as well as the chloride. If lithium chloride is used, it supplies a part of the halide, the remainder being sodium or potassium chloride, iodide or bromide. Fluorides alone are not satisfactory, although lithium fluoride may be used as a source of lithium provided an alkali-metal salt of another halogen is also present. The oxidizer may be a hydroxide, peroxide, chromate, phosphate, molybdate or vanadate, as well as a carbonate.

As to proportions, the lithium ion content should be not less than 0.7 weight percent, which, in a typical bath is supplied by a lithium chloride content of 4.25%. The preferred lithium ion concentration is about 1% (6% Li Cl) but it may be as high as 6.6% (40% Li Cl). The concentration of the oxidizing ion should be not less than about 0.3 weight percent, and preferably not over about 36 weight percent, concentrations between 2% and 27% being preferred.

The more commonly used halogen suppliers are potassium and sodium chloride, and the most convenient oxidizers are potassium and sodium carbonate. With 6% weight lithium chloride,

these may be used in all combinations and wide ranges of proportions, as follows:

|                          | Weight<br>Per Cent | Weight<br>Per Cent | Weight<br>Per Cent | Weight<br>Per Cent |
|--------------------------|--------------------|--------------------|--------------------|--------------------|
| Lithium Chloride.....    | 6 -15              | 6 -30              | 6-30               | 6 -15              |
| Potassium Chloride.....  | 10 -93             |                    | 30-93              |                    |
| Potassium Carbonate..... | 0.5-84             |                    |                    | 2.3-69             |
| Sodium Chloride.....     |                    | 30 -93             |                    | 25 -92             |
| Sodium Carbonate.....    |                    | 0.5-64             | 1-64               |                    |

Other effective baths are as follows:

Various halogens and lithium salts:

|                         |      |      |      |      |    |    |
|-------------------------|------|------|------|------|----|----|
| Sodium carbonate.....   | 47.6 | 44.2 | 43.8 | 46.3 | 45 | 47 |
| Potassium chloride..... | 47.6 | 44.2 | 43.8 | 46.3 | -- | -- |
| Potassium bromide.....  |      |      |      |      | 45 | -- |
| Potassium iodide.....   |      |      |      |      | -- | 47 |
| Lithium fluoride.....   | 4.8  |      |      |      | -- | -- |
| Lithium carbonate.....  |      | 11.6 |      |      | -- | -- |
| Lithium phosphate.....  |      |      | 12.4 |      | -- | -- |
| Lithium bromide.....    |      |      |      | 7.4  | 10 | -- |
| Lithium chloride.....   |      |      |      |      | -- | 6  |

Various oxidizers:

|                         |    |    |    |    |    |    |
|-------------------------|----|----|----|----|----|----|
| Potassium chloride..... | 84 | 90 | 84 | 84 | 84 | 84 |
| Lithium chloride.....   | 6  | 6  | 6  | 6  | 6  | 6  |
| Sodium hydroxide.....   | 10 | -- | -- | -- | -- | -- |
| Sodium peroxide.....    | -- | 4  | -- | -- | -- | -- |
| Sodium chromate.....    | -- | -- | 10 | -- | -- | -- |
| Sodium phosphate.....   | -- | -- | -- | 10 | -- | -- |
| Sodium vanadate.....    | -- | -- | -- | -- | 10 | -- |
| Sodium molybdate.....   | -- | -- | -- | -- | -- | 10 |

The surface film which forms on titanium and its alloys, when immersed in the salt baths above-described, is extremely thin, iridescent, and of a purple-to-black color. It has been found to contain titanium dioxide and lithium titanate, as well as compounds not identified. Its major constituent is titanium. It also contains a small percentage of lithium, and only low traces of other elements identifiable by spectrograph analysis. By the use of sodium hydride it is readily removed as desired, for further processing or surface finishing of the metal.

What is claimed is:

1. In the processing of titanium and its alloys, the method which comprises treating the metal with a molten salt composition at a temperature between 1200° F. and 1600° F., said composition consisting essentially of ions of lithium in a concentration between 0.7% and 6.6%; ions selected from the group consisting of chloride, iodide and bromide; and oxidizing ions capable of forming a titanate at the working temperature.

2. In the processing of titanium and its alloys, the method which comprises treating the metal in a molten salt bath, said bath consisting essentially of a material selected from the group consisting of lithium and its compounds in such an amount as to provide a lithium ion concentration of from 0.7% to 6.6%, a material selected from the group consisting of the chlorides, iodides and bromides of potassium and sodium, and an oxidizing material selected from the group consisting of hydroxides, peroxides, carbonates, chromates, phosphates, molybdates and vanadates.

3. In the processing of titanium and its alloys,

the method which comprises treating the metal in a molten salt bath, said bath consisting essentially of a halogen salt of lithium in such an amount as to provide a lithium ion concentration of from 0.7% to 6.6%, a halogen salt of another alkali metal selected from the group consisting of chlorides, iodides and bromides, and an oxidizing salt selected from the group consisting of the peroxides, hydroxides, carbonates, chromates, phosphates, molybdates and vanadates of sodium and potassium.

4. In the processing of titanium and its alloys, the method which comprises treating the metal in a molten salt bath, said bath consisting essentially of a lithium salt in such an amount as to yield a concentration of lithium ions between about 0.7 and about 6.6 weight percent, a carbonate in such an amount as to yield a carbonate ion concentration between about 0.3 and about 36 weight percent, balance an alkali-metal salt selected from the group consisting of chlorides, bromides and iodides.

5. In the processing of titanium and its alloys, the method which comprises treating the metal in a molten salt bath at a temperature between 1200° F. and 1600° F., said bath consisting essentially of between about 6% and about 30% of lithium chloride, between about 0.5% and about 64% of sodium carbonate, and the remainder a chloride selected from the group consisting of the chlorides of sodium and potassium.

6. In the processing of titanium and its alloys, the method which comprises treating the metal in a molten salt bath at a temperature between 1200° F. and 1600° F., said bath consisting essentially of between about 6% and about 15% of lithium chloride, 0.5% to about 84% of potassium carbonate, and the remainder a chloride selected from the group consisting of the chlorides of sodium and potassium.

7. In the processing of titanium and its alloys, the method which comprises treating the metal in a molten salt bath at a temperature between 1200° F. and 1600° F., said bath consisting essentially of about 47% sodium carbonate, about 47% potassium chloride, and about 6% lithium chloride.

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