



## Boride coatings obtained by pack cementation deposited on powder metallurgy and wrought Ti and Ti–6Al–4V

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### ABSTRACT

Wear resistance of Ti alloys needs to be improved, and an effective way to achieve this is through surface treatment. Boronizing is a surface treatment in which boron diffuses into the surface of Ti leading to the formation of hard and wear-resistant Ti borides. Boronizing of wrought and/or cast Ti alloys by pack cementation has been studied, while similar coatings on Ti alloys produced by powder metallurgy (PM) have not been reported. Also critical process parameters for boronizing Ti alloys, such as pack cementation powder composition and the process temperature have not been systematically studied and analysed. The present work reports on the surface modification of PM Ti and PM Ti–6Al–4V by boronizing, and presents some important thermodynamic aspects of the process comparing it with similar coatings applied to wrought Ti–6Al–4V. The coatings were characterised using scanning electron microscopy and X-ray diffraction. For both Ti and Ti–6Al–4V alloys the use of amorphous B as a B element supplier in the boriding powder pack led to the formation of a uniform external boride layer, while the use of B<sub>4</sub>C as a B element supplier in the pack and under the same boronizing conditions, led to the formation of an external TiN layer and an internal layer containing B. The thermodynamic calculations performed proved successful in determining the appropriate conditions for boride coating deposition and estimating the phases likely to be formed. Finally the effect of surface roughness on the coating quality is discussed.

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### 1. Introduction

Ti alloys are used in the aerospace, automotive, power generation, chemical, marine, biomedical and sports industries, due to their excellent combination of mechanical properties with low density and corrosion resistance. A limitation for the wider use of Ti alloys in engineering applications is their poor tribological and wear behaviour. Surface modification seems to be an effective way to improve the tribological and wear properties of Ti alloys and various methods including PVD [1], CVD [2], laser, plasma surface treatments [3–5], ion nitriding [6] and solid state diffusion [7] have been used to improve their wear performance.

Comparing the different surface modification methods, limitations exist in terms of the thickness of layers, process complexity, cost, component geometry and the final quality and properties of the coatings obtained. Solid state diffusion through pack cementation is a widely used low cost, simple and flexible process, allowing complex geometry components to be coated. The pack cementation process consists of placing the material to be coated in a sealed or semi-sealed container which contains a powder mixture of the metal elements to

be deposited, halide activators and an inert filler. The container is heated under a protective atmosphere to temperatures of 700–1150 °C and held there for a specified duration. The chemical vapors are generated in-situ and the coating is formed by chemical reaction of the halide vapors at the metal surface and subsequent diffusion of the metal elements into the substrate. The composition and properties of the coating are sensitive to the process parameters, such as the powder mixture composition, substrate composition, temperature and time, which can be varied to produce the desired coating. Both pure Ti and Ti based alloys have been boronized using this method in order to improve their oxidation and wear performance. Boronizing of Ti and/or Ti alloys by pack cementation has been reported [7–10] using a variety of pack cementation powder mixtures in the temperature range of 800–1100 °C. Aich S. [7] boronized Ti using a powder mixture of amorphous B anhydrous, sodium carbonate and activated charcoal, at temperatures ranging between 800 and 1100 °C, for periods of 1–24 h, obtaining dual coatings of TiB<sub>2</sub>/TiB whiskers, with thickness between 10 and 78 μm. The kinetics, nature of growth and quality of this dual TiB<sub>2</sub>/TiB whiskers layer have been critically examined by Tikekar N. M [8]. More recently Lee C. reported [9] on the improved tribological properties of Ti–Al–V alloy coated with a dual TiB<sub>2</sub>/TiB whisker layer. The boronizing powder mixture was reported to contain a B source, an activator and a dioxidant, and boronizing was carried out at 1050 °C for 24 h. Improved tribological properties of borided Ti–Al–V were also reported by Atar E. [10]. Boronizing in this

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case was done at 1100 °C for 2 h using a commercially available powder mixture and resulting in a TiB<sub>2</sub>/TiB layer.

To our knowledge no boronizing treatment has been reported on Ti alloys produced by powder metallurgy methods. The differences in the microstructure, surface porosity, and surface roughness of PM Ti and Ti alloys compared to that of wrought Ti alloys will influence the characteristics of the obtained coating. Furthermore it is unclear how the different powder mixture compositions, temperatures and times of treatment influence the type, nature and quality of the final boride coatings. In this work we present the results of boronizing treatments of Ti and Ti alloys produced by powder metallurgy coupled with thermodynamic analysis using Thermocalc computer software program [11] in an effort to better understand the thermodynamics of the boronizing process.

## 2. Material and methods

### 2.1. Target materials

The composition of the substrates was pure Ti and the Ti6Al4V alloy (Ti – 6 wt.% Al – 4 wt.% V). The substrates were produced by the conventional powder metallurgy route. Green compacts of about 16 mm in diameter and 3 mm in thickness were obtained in a uniaxial die under a pressure of 600 MPa, using Zinc stearate as a wall-die lubricant. The samples were subsequently sintered under vacuum for 2 h at 1200 °C. In addition, substrates made of wrought laminated Ti alloy with composition Ti – 6 wt.% Al – 4 wt.% V (Ti6Al4V) and dimensions of about 10×15×1 mm were also used. All samples were ultrasonically cleaned in alcohol, dried and weighed prior to the coating experiment.

### 2.2. Thermodynamic calculations

Thermodynamic studies of the phase equilibrium during the coating deposition process were performed using Thermocalc software [11] to determine the feasibility of metal deposition and provide useful guidelines to optimize the coating conditions. Calculations are based on the free Gibbs energy minimization code, in combination with SSUB4 database (Scientific Group Thermodata Europe).

### 2.3. Coating procedure

The pack powder mixtures were prepared weighing and mixing appropriate amounts of powders of the metal donor, inert filler material and halide salts (activators). The standard procedure included mixing the weighted powders in a tubular shaker for 30 min. The activator used was NH<sub>4</sub>Cl. The metal donors used were anhydrous amorphous B (99.5% purity) and B<sub>4</sub>C (99.5% purity). Al<sub>2</sub>O<sub>3</sub> was used as inert filler. The pack mixture was placed in an alumina crucible and the samples were inserted in the pack mixture. The crucible was placed inside a semi-airtight refractory metal box that contained a gas entry and a separate gas exit orifice as well as a thermocouple for controlling the temperature. The box was placed inside a muffle type furnace. Before the main pack cementation process the pack was purged with argon and the temperature was raised to and held at 100 °C for 1 h to remove moisture. The furnace temperature was then raised to the final coating temperature of 950 °C and was held at this temperature for 6 h. The argon atmosphere was maintained throughout the whole heating cycle. The furnace was then cooled to room temperature at its natural rate by switching off its power supply while maintaining the argon gas flow. In order to avoid oxidising, oxygen-getters consisting of porous samples of pure titanium were placed in the crucible to react with any oxygen present.

### 2.4. Characterisation techniques

Surface roughness of the powder metallurgy and the wrought samples was measured using a contact surface profilometer and the values for R<sub>a</sub> and R<sub>q</sub> were obtained. X-Ray diffraction analysis using monochromatic Cu K<sub>α</sub> radiation (Philips X'PERT MPD) was performed in order to identify the phase composition of the coated samples. The cross section of the coated samples was characterised by scanning electron microscopy (SEM Phillips) and energy dispersive X-Ray spectroscopy (EDX). Prior to cutting the coated samples a Nickel layer was applied by electroless deposition in order to protect the underlying coating during metallographic preparation. Standard metallographic preparation was performed on samples prior to cross section observations.

## 3. Calculation

The main steps involved in a pack cementation process are as follows. Gaseous reactant species (precursors) are formed by reaction of the activators with the metal donor contained in the powder mixture. Upon reaching the heated sample, the gas precursors are absorbed and react at the surface to form a stable solid film of the metal to be deposited. Subsequently, the coating is formed by reaction–diffusion between the metal to be deposited and the substrate. Gaseous by-products are recombined and de-absorbed into the gas phase. Diffusion in the gas and/or solid phases rather than the surface reaction is thought to be rate controlling [12–16]. The effectiveness of different activators and metal donors in transferring and depositing from the packs to the different substrates depends essentially on the amount/partial pressures of gas precursors that they generate within the packs at the coating temperature, which, in turn, depends on the compositions of powder mixtures. Thermodynamic equilibrium calculations of the gas species formed at high temperatures for different pack compositions were performed in order to determine the appropriate pack composition for boride coating deposition. In order to perform a preliminary analysis of the thermochemistry, initially, assumptions were made about the amount of activators and metal donors needed in the pack, based on the usual amounts used in the pack cementation processes.

Fig. 1a shows the gas composition created for a pack mixture containing 20 wt.% amorphous B and 3 wt.% NH<sub>4</sub>Cl activator deposited at atmospheric pressure as a function of temperature. The inert Al<sub>2</sub>O<sub>3</sub> filler was not taken into consideration in the calculation. It is observed that with increasing temperature the partial pressure of the gas precursors increases. For temperatures above about 800 °C the partial pressure of gas precursors generated is within the range required usually for successful deposition of similar coatings by pack cementation or CVD processes [17,18], although the optimum ranges for deposition of boride coatings on titanium-based substrates have not been reported. The produced gases include boron chlorides, boron hydrides, hydrogen gas, Cl and HCl gas (some gas species that do not contain B are not plotted for simplicity; NH<sub>3</sub> and Cl<sub>2</sub> are present at high temperatures and it is possible that small quantities of these gases might react with the substrate material). The presence of all these compounds (HCl, Cl, hydrogen gas, boron hydrides and NH<sub>3</sub>) is expected to play a significant role in the boronizing process and the coating quality.

For a pack containing 20 wt.% B<sub>4</sub>C as a metal donor instead of amorphous B, the gas composition of a pack mixture containing 3 wt.% NH<sub>4</sub>Cl was also calculated as a function of temperature and it is presented in Fig. 1b (some gas species that do not containing B are not plotted for simplicity; NH<sub>3</sub> and Cl<sub>2</sub> are present at high temperatures). The gas species generated are the same as the gas species generated when amorphous B is used as a metal donor. Therefore, it appears that in the temperature range of 800 °C–1100 °C, which is normally used for boronizing Ti alloys there would be no significant influence in

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