Future trends in gaseous surface hardening of titanium and titanium alloys

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Future trends in gaseous surface hardening of titanium and titanium alloys

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An overview of existing surface hardening techniques applicable for titanium and titanium alloys with special emphasis on gaseous based processes is provided. New processes for gaseous surface hardening of titanium alloys and zirconium are presented. This entails low temperature oxidizing by chemically controlled partial pressures of oxygen resulting in deep and hard diffusion zones and the possibility for applying so-called mixed-interstitial phases for surface hardening. Mixed-interstitial phases (based on carbon, oxygen and nitrogen) can result in new intriguing microstructural features and properties in case-hardened titanium. Deep and very hard cases can be produced by these new techniques. Hardness values of metallic titanium of more than 1800 HV is possible by simultaneously dissolving three interstitial elements. Mixed-interstitial compounds based on oxygen and carbon can lead to hardness values in the range of 2000 to 3000 HV. Finally, examples of surface hardening of metal 3D printed parts in titanium grade 5 are shown.

KEYWORDS: TITANIUM – SURFACE HARDENING – NITRIDING – OXIDATION – CARBO-OXIDATION - MIXED INTERSTITIAL PHASES

INTRODUCTION: TITANIUM – THE EXOTIC METAL AND AN ENGINEERING MATERIAL

Titanium is a rather unique material due to its high specific strength, low density, excellent corrosion resistance and its inherent biocompatibility. Historically, titanium was developed in the 1940's and 50s as a technological material. In the early days of titanium development (1930 and 1940's) there were indeed visions of a new light weight, high strength and highly corrosion resistant engineering material that could be used instead of steel; it was contemplated that everything could be constructed of titanium, e.g. bridges etc. Here, the "wonder metal" still lacks its major breakthrough. The development was highly driven by the Cold War weapons race in the wake of the Second World War. Popularly speaking, the Americans developed and used it for (military) aerospace and the Russians for making sub-marines. Many of the, today, well-known titanium alloys were actually developed in that period – mainly for military use. Today, titanium alloys are used in a plethora of different applications and industries spanning from sports equipment over chemical industry to bio-medical applications. Titanium has two different crystal forms: up to 882°C it is hexagonal (h.c.p.), α-Titanium, and above 882°C it is body centered cubic (b.c.c.), β-Titanium. This transition between alpha and beta is denoted the transus temperature and is highly composition dependent. The interstitial elements carbon, oxygen and nitrogen are strong alpha-stabilizers whereas hydrogen stabilizes beta. The substitutional elements can be categorized into both alpha and beta stabilizers. Conventionally, titanium alloys are classified according to their structure, i.e. from commercially pure titanium (CP), near-alpha, alpha/beta, metastable beta and stable beta alloys. The beta alloys (containing beta stabilizers) can further be subdivided into alloys which contain eutectoid forming alloying elements (typically hardenable beta alloys) and beta alloys containing isomorphous alloying elements. One of the best known titanium alloys is the alpha/beta titanium alloy Ti6Al4V (grade 5) which can be heat treated to obtain high strength, analogous to treatment of steels, i.e. hardenable by a martensitic transformation and/or by (subsequent) ageing.

The possibility to obtain high strength in a low density material (high specific strength) makes titanium alloys particularly relevant in aerospace applications. It is not always realized that the introduction of new (commercial) airplanes containing composites actually entails more use of titanium alloys, as the conventional

aluminum alloys are incompatible with carbon fibers due to corrosion issues. For biomedical implants the material of choice has shifted to being titanium based materials at the expense of stainless steels and cobalt based materials, owing to its excellent biocompatibility. Moreover, the advent of additive manufacturing techniques such as 3D metal printing is also giving a renaissance to titanium, as 3D metal printing is widely based on titanium (powders). However, one of the weaknesses of titanium is its price – it is significantly more expensive than, say, stainless steels. The relatively high price of titanium is due to the costly extraction and production process, viz. the Kroll process. Actually, the element titanium is highly abundant in the earth's crust (seventh most abundant metal) but it is chemically bound as minerals (oxides). Hence, metallic titanium is difficult to produce due to the high reactivity of the element and the propensity to form oxide (it has somewhat derisively been called the "street walker metal", as it picks up everything!).

A major shortcoming of titanium, which effectively hinders its use in many applications, is its poor wear resistance and tribological properties. Titanium cannot be used in applications that involve wear and in many existing applications poor wear performance is only accepted because of its highly favorable corrosion properties. For example, in biomedical implants titanium can be exposed to fretting, resulting in wear particle debris which can be detrimental for the performance of the implant. In order to remedy this inherent problem with titanium, *surface hardening* can be applied.

Nitriding

Gaseous nitriding of titanium is the classical way to obtain high surface hardness and improved wear resistance. The process was introduced in the 1950's and entails the use of relatively high temperatures (e.g. 900 to 1000°C) and high purity gas, typically N_2 (NH_3 can also be used) [1,2]. The surface is transformed into TiN, which has a golden color; this compound is supported by a layer of Ti_2N and an underlying diffusion zone where nitrogen is dissolved in metallic titanium. The solubility of nitrogen in titanium is significant, so the diffusion zone can possess a hardness of up to, say, 900 HV; the TiN layer is in the range 1800-2100HV, albeit relatively thin. This process is in many ways excellent as the surface layer of TiN is chemically anchored to the substrate (contrary to deposition processes such as CVD or PVD) and is supported by a relatively hard diffusion zone. Moreover, the friction coefficient of the TiN layer is low compared to untreated titanium. However, the material looks like gold, which can be undesirable for many applications. In addition, the total affected depth (hardened zone) is relatively shallow, e.g. 25-50 µm. Also, the fatigue performance can be negatively affected by having the hard and thin TiN layer.

Oxidation

Oxidation or oxidizing is usually considered as something highly detrimental, i.e. formation of oxide scales is typically unwanted. In the titanium industry, the dissolution of oxygen in titanium during processing is normally considered as "contamination" and referred to as (unwanted!) "oxygen pick-up". Hence, counterintuitively oxygen *can* be used for surface hardening. Titanium is rather unique when it comes to oxygen as it possesses a very high solid solubility of oxygen (up to 33 at.%). Oxygen is also an effective solid solution strengthener, which makes it possible to obtain a high hardness (e.g. in a diffusion zone). Titanium and oxygen also form a range of different oxides, which typically are not as hard as the titanium compounds based on carbon or nitrogen. Hence, in order to apply oxygen as a hardening element the formation of a surface oxide layer should be avoided. This can be extremely difficult as it requires very low equilibrium partial pressures of oxygen. Work on surface hardening of titanium with oxygen as the hardening element was published already in the 1960's [3]; here a molten glass was used as a medium for supplying oxygen to the solid state resulting in significant hardening. Subsequent annealing processes were also performed, i.e. "boost" processing. Several other publications exist where oxygen has been used for surface hardening - a range of different process conditions have been applied. Also, gaseous boost processes have been shown to be effective in surface hardening [4]. It can be exploited that titanium will re-dissolve its own oxide layer at temperatures above approximately 550°C (provided that supply of oxygen from the gas phase is hindered, i.e. high vacuum). The boost process consists of oxidation by formation of a (thick) rutile oxide layer which is redissolved in a vacuum post treatment step. The oxygen rich rutile layer acts as a reservoir for oxygen for inward diffusion (into metallic titanium). Case depths of a few hundred micrometers and hardnesses up to 900-1000 HV can be achieved.

Carburising
Carburising is rather niche as a surface hardening process for titanium as it requires very high temperatures and an appropriate gas system that can exclusively provide the carbon. The solubility of carbon in titanium is very low compared to oxygen and nitrogen; on the other hand, the compound TiC is very hard. The low solubility of carbon entails a very limited load bearing capacity for the very hard (and thin) TiC compound. This situation can result in an eggshell effect. Hence, carburizing is not a real option for surface hardening.

Other processes
There is a range of other processes for surface hardening of titanium. There are deposition processes, such as PVD and CVD, numerous variants of plasma/ion-based/assisted processes and laser assisted types; these will not be discussed here.

The 4th interstitial element, not mentioned so far, is boron which forms extremely hard titanium borides - these are even harder than the carbides. Boriding cannot be performed directly as a gas-based process due to the toxicity of boron-containing gases. Therefore, boriding of titanium is typically performed as a powder pack process, where the donating gasses are produced “in-situ”. Powder pack boriding requires high temperatures, typically more than 1000°C or more, and dictates that parts have to be embedded in powder during processing. The boron solubility in titanium is rather low which means that a situation analogous to carbon exists; the formation of a hard thin layer on a soft substrate.

It is also possible to combine different interstitial systems, i.e. to produce layers containing so-called mixed interstitial phases. Work by Fedirko et al. [e.g. 5] has clearly shown that layers containing several interstitials can have intriguing properties. Mixed phases can have different chemical and physical properties compared to the “pure” systems; this is also something that is exploited for titanium based coatings (CVD & PVD). Recent research in the authors’ lab has also shown new possibilities of using mixed interstitial phases [6,7]. Again, titanium has a special behavior: the isomorphous rock-salt type compounds TiC, TiN and TiO ostensibly exhibit intersolubility between the different series (when in equilibrium), i.e. carbon, nitrogen and oxygen can substitute each other. However, these ternary and tertiary systems have not been fully investigated. Moreover, mixed interstitial solid solutions in titanium (solubility in metallic alpha titanium) are also possible. Early work by Stone and Magolin [8] has indeed indicated augmented interstitial solubility by combining interstitials. High interstitial solubility can result in an enhanced strengthening effect and can be exploited for surface hardening. Hitherto, the synergistic effects in mixed-interstitial phases in the titanium system have not been well investigated.

The remainder of this article is intended to provide, in a kaleidoscopic way, some *snapshots* of ongoing research on surface hardening of titanium in the authors’ lab. In particular, emphasis is on the possibilities of using mixed interstitial phases for surface hardening and the possibility of applying controlled gaseous conditions. Several of the processes are currently proprietary and in the progress of being patented, thus some process details are deliberately left out. General details of the processes and materials are provided in the figure captions throughout.

NEW GASEOUS SURFACE HARDENING PROCESSES

Chemically controlled oxidation
Oxidation as a surface hardening method has the potential to enhance the surface hardness of metallic titanium significantly due to the very high solid solubility of oxygen in titanium and due to the effectiveness of oxygen as an interstitial strengthener. However, this comes at the expense of ductility (but this is the classical trade-off in many surface engineering processes). The partial pressure of oxygen, which is required to avoid or suppress formation of unwanted oxide (viz. rutile TiO_2), is extremely low. Hence, it is impossible to achieve a *physical* pressure, which is low enough to avoid formation of oxide (thermodynamically speaking). However, the formation of a surface oxide is a flux- or mass balance between the imposed pressure and related surface kinetics and transport into the material by diffusion. This means that a kinetically controlled process, where the flux of oxygen determined by the imposed (low) pressure equals the inward diffusion flux in the solid state, can

in principle be established, but will in reality be difficult to control. In Fig.1 a different approach for oxidation of titanium in a controlled way has been adopted. Here a chemically controlled partial pressure is established at atmospheric pressure. The process is operated under controlled conditions where the partial pressure of oxygen is adjusted and kept at $pO_2 = 2.8*10^{-22}$ bar by controlling the gas composition in the reactive gas system.

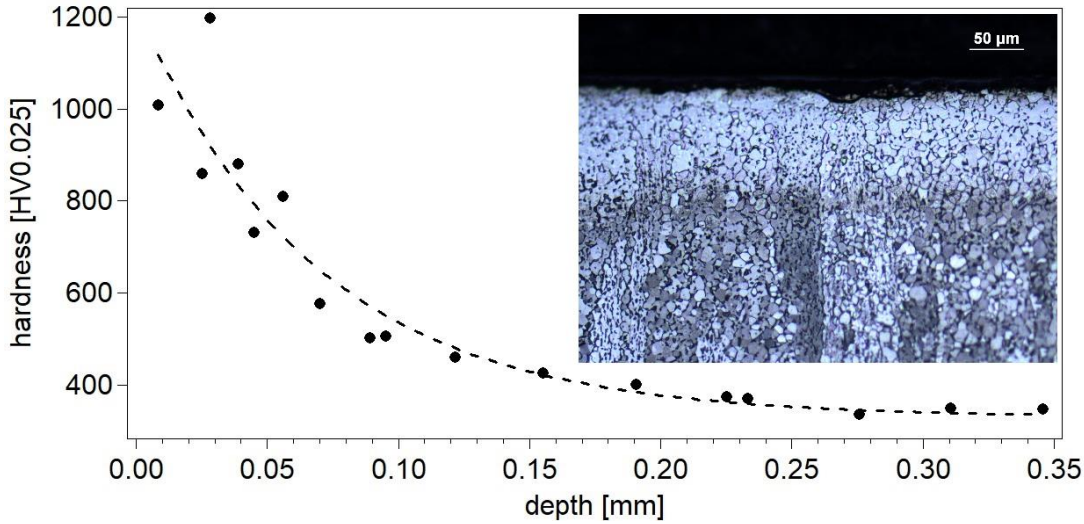

Fig.1 Surface hardening of titanium grade 5 with a low oxidizing temperature (60 hours 690°C) using a chemically controlled (low) partial pressure of oxygen of $2.8*10^{-22}$ bar. Micrograph of the hardened case consisting of a diffusion zone (oxygen in solid solution). Hardness depth profile showing that the hardness is positively affected to a depth of almost 200 µm [9].

The micrograph in Fig.1 shows the microstructure of a titanium grade 5 component with an equi-axed structure (alpha grains surrounded by minor fractions of partly decomposed beta). The low temperature applied (690°C) does not affect the overall microstructure. The process results in a thick diffusion zone of oxygen dissolved in the alpha titanium; it is not fully clear if the beta regions have been transformed into alpha due to dissolution of oxygen, which is a strong alpha stabilizer. The hardened zone extents to a depth of more than 150 µm; the surface hardness is close to 1200 HV, which is higher than what can be achieved at higher temperatures for this alloy and higher than what can be obtained in CP titanium. The presence of aluminum in the alloy is likely to have a beneficial effect at the relatively low surface hardening temperature due to its high affinity to oxygen. This type of process can also be performed under different process conditions, e.g. at higher temperatures, shorter durations etc.

Fig.2 shows an example of surface hardening CP titanium grade 4 by a boost type process. The part was firstly treated at low temperature in a highly oxidizing atmosphere to obtain a shallow diffusion zone with a relatively thick, dense and hard oxide layer. This resulted in an anthracite-like surface finish. Secondly, the part was treated in a vacuum at a slightly higher temperature in order to redissolve the oxide and redistribute the oxygen; this results in a diffusion zone which extents more than 40 µm into the material. The surface finish of this duplex treated part is shiny metallic and unaffected by the treatment. The hardness profile (Fig.2) has a smooth gradual transition from the high surface hardness of approximately 900 HV to the hardness of the core of approximately 250 HV.

Controlled (chemical) oxidation of zirconium is also possible as it is highly similar to titanium, i.e. it has an even higher solid solubility of oxygen. Zirconium is somewhat more exotic than titanium (as a metal), but is currently considered as an attractive material for implants. Fig. 3 shows an example of surface hardened zirconium using an oxidation treatment with a chemically controlled partial pressure of oxygen. The hardened case consists of a hard ZrO_2 compound layer at the surface supported by a diffusion zone where oxygen is in solid solution in zirconium. Contrary to titanium, zirconium forms a dense, well-adhering and hard oxide (ZrO_2). The

conditions applied in Fig.3 are intended to deliberately produce ZrO_2 having a hardness of around 1200 HV.

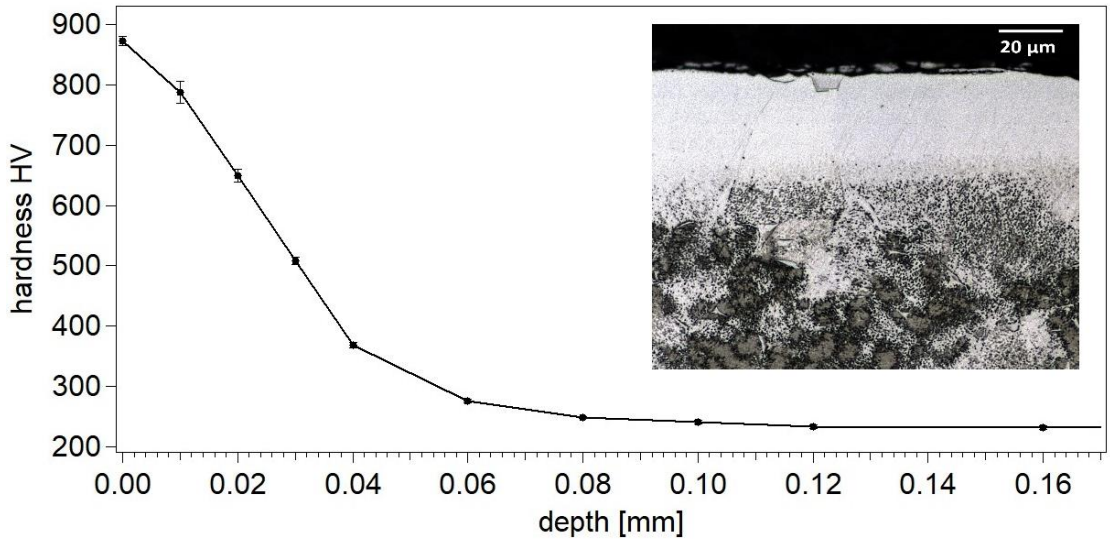

Fig.2. Surface hardening of CP titanium grade 4 dental implant part by a duplex hardening process: controlled low temperature oxidation with a high oxygen partial pressure followed by vacuum treatment for redistribution of oxygen and concomitant dissolution of the (thin) oxide layer. The surface is metallic bright after the treatment. Micrograph of the hardened case and corresponding hardness depth profile.

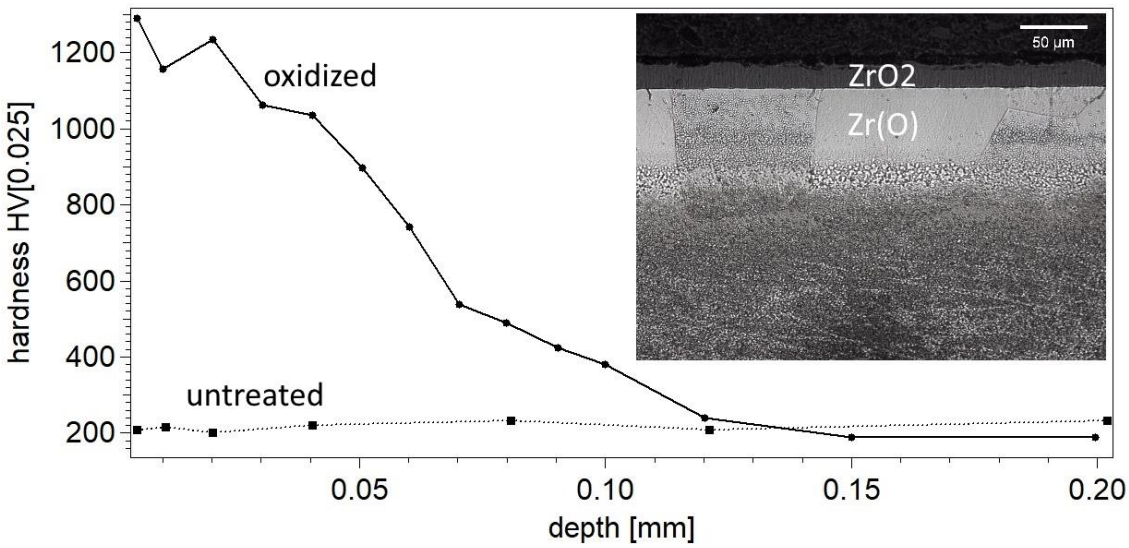

Fig.3. Surface hardening of zirconium by oxidation treatment (12 hours at 820°C using a chemically controlled partial pressure of oxygen of $1.2*10^{-18}$ bar). Micrograph and corresponding hardness depth profile. The surface consists of a dense and hard layer of ZrO_2 supported by a relatively thick diffusion zone where oxygen is dissolved in Zr [10].

Mixed-interstitial phases; multiple interstitial elements

So far only single element hardening has been shown (oxygen), but there is also the possibility of mixed-interstitial phases, i.e. mixed compounds and solid solutions. Surface hardening by mixed interstitial compounds typically requires higher temperatures, i.e. above the beta transus temperature. This also implies that the core microstructure is affected. Fig. 4 shows examples of carbo-oxidation of CP titanium grade 2, i.e. simultaneous incorporation of both carbon and oxygen. Clearly, very thick hardened layers are obtained at the applied temperatures (1000°C and 1050°C). The case resulting from carbo-oxidation consists of a diffusion zone where carbon and oxygen is dissolved in (α) titanium and a compound layer or network where a mixed

interstitial rock-salt type compound, TiC_xO_{1-x} has formed. The exact ratio between carbon and oxygen in solid solution and in the compound is presently not fully determined; however, preliminary thin foil experiments indicate that a ratio close to 50:50 is obtained (overall average in the foil).

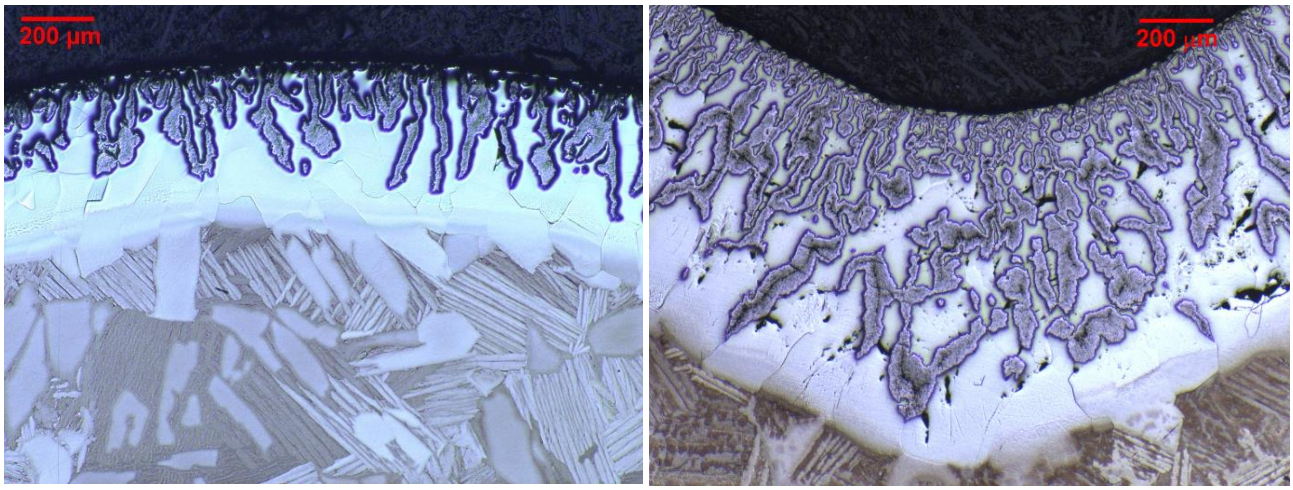

Fig.4 – Micrograph of a surface hardened (carbo-oxidation) of titanium grade 2. Left) 20 hours at 1000°C; Right) 20 hours at 1050°C. The hardened case consists of a diffusion zone (C and O dissolved in the titanium) and a carbo-oxide compound zone / network ("stringers"). The hardness of the diffusion zone can reach up to 1500 HV depending on treatment and the compound zone (carbo-oxide) spans over a broad hardness range, say, 2000 to 3000 HV. The hardness of the compound zone relies heavily on process parameters and titanium alloy composition.

The hardness of the mixed compound depends strongly on the applied process conditions, i.e. values in the range 2000 to 3000 HV (or slightly higher) have been measured. In the two shown examples in Fig.4 the hardness of the compound is in average around 2500 HV. The diffusion zone, i.e. metallic titanium with dissolved interstitials, has a hardness of up to 1500 HV, which is significantly harder than what can be obtained using single interstitial elements (e.g. dissolving just oxygen). The growth of the hardened case is much faster than what is observed for nitriding and oxidizing (as stand-alone treatments). The hardened case can also be considered as a kind of composite, where a very hard phase (the compound TiC_xO_{1-x}) is "embedded" in a "softer" matrix phase (where the interstitials are in solid solution). The core structure has undergone a transformation because of treatment in the beta temperature range: it consists of lamellar alpha or Widmanstätten structure. These microstructural forms are harder than the equi-axed alpha form.

Fig 5. shows examples of carbo-oxidation of two different titanium alloys, i.e. titanium grade 5 and the beta implant alloy Ti13Nb13Zr (TNZ). The titanium grade 5 alloy has a largely different response to the treatment than the CP titanium alloys. The carbo-oxide compound layer takes a different morphology and forms uniformly at the surface. This can be attributed to the presence of aluminum, which is a stronger oxide former than titanium. Moreover, aluminum is likely not to reside in the rock-salt structure of the carbo-oxide compound layer, which implies that redistribution occurs. Such redistribution can be rate determining for the growth of the carbo-oxide layer. However, the exact behavior needs further investigation. The TNZ alloy has been developed for use in implants. It has a low E-modulus, which is more compatible with the human bone (stress shielding effect). Interestingly, the response of this material resembles CP titanium and yields a dense layer of carbo-oxides at the surface. These carbo-oxides develop within the diffusion zone where carbon and oxygen are in solid solution. The core does not seem to be affected by the treatment based on the microstructure, but it has a hardness of approximately 1000 HV, which hints at a hardening effect from interstitials. It is suggested that this is due to interstitials dissolved in beta (the presence of alloying elements in titanium can enhance the interstitial solubility in beta). Applying mixed interstitials may also result in synergistic effects on (beta) solubility. Again, further investigation is needed.

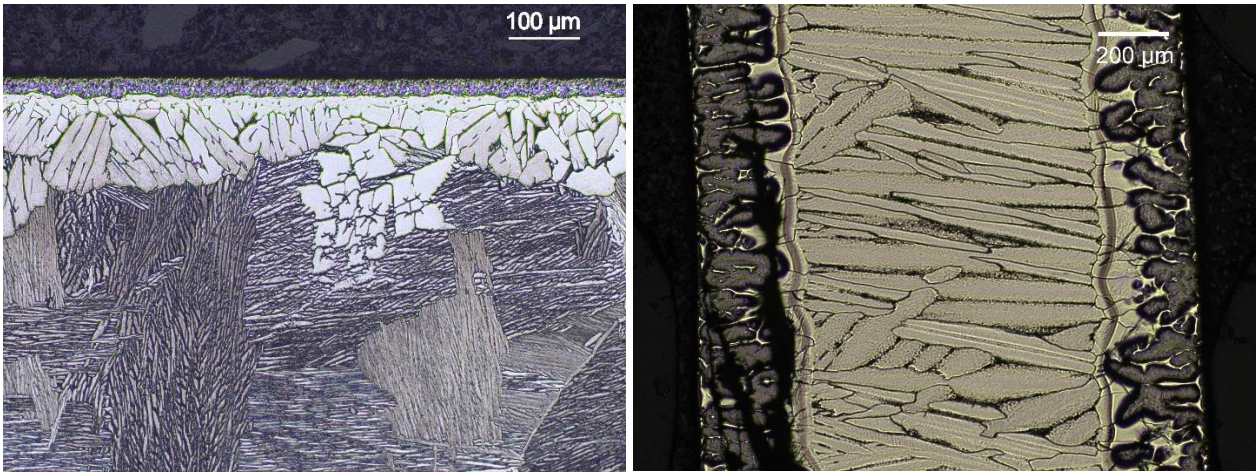

Fig.5 – Micrographs of a surface hardened titanium alloys (carbo-oxidation). Left) Titanium grade 5 carbo-oxidized for 2 hours at 1000°C [9]. The hardened case consists of a uniform compound layer (carbo-oxide) at the surface supported by a diffusion zone with mainly oxygen in solid solution. Right) The implant beta alloy Ti13Nb13Zr carbo-oxidized for 2 hours at 1050°C [10]. The hardened case consists of a zone with dense rounded carbo-oxide compounds in a diffusion zone; the core has a hardness of 1000 HV, which suggest the presence of interstitials.

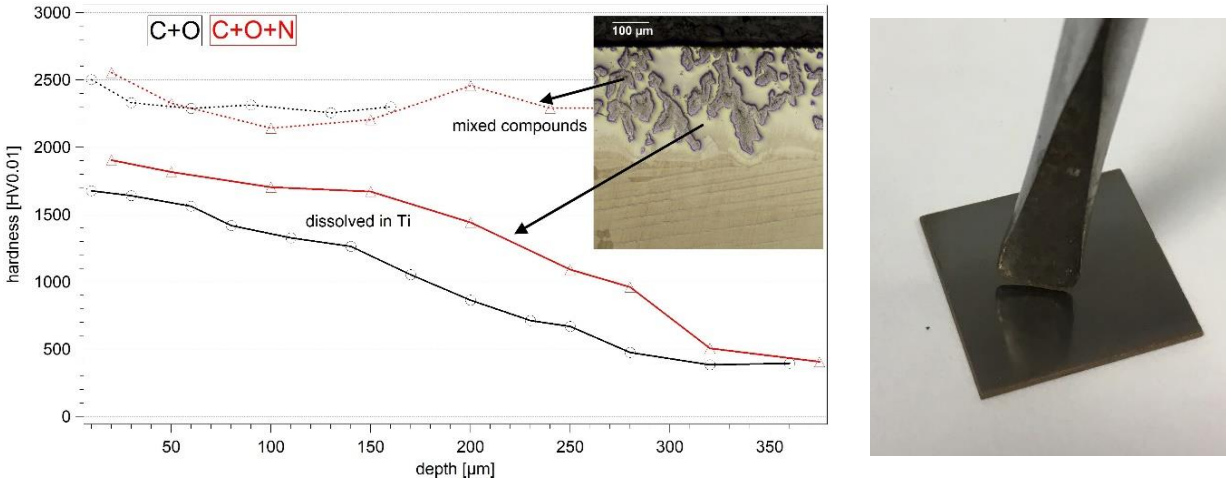

Fig.6. Surface hardening of titanium grade 2. Hardening effect of three interstitial elements, i.e. carbon, oxygen and nitrogen. The sample was initially carbo-oxidized followed by nitriding. Left) hardness depth profile and corresponding micrograph. The hardness depth profiles are subdivided into two profiles: one for the compound region and one for the diffusion zone (interstitials dissolved in the titanium). The effect of adding all three interstitial elements is a very high hardness in the metallic titanium, reaching almost 1900 HV. A carbo-oxidation treatment is shown for comparison. Right) Photo of a treated (three interstitials) and mirror-polished specimen. The surface is extremely scratch resistant; even brute force using a mechanical tool will not affect the surface [11].

It is also possible to introduce three interstitial elements into titanium, which can be done simultaneously (nitro-carbo-oxidation) or by combining carbo-oxidation with pre- or post nitriding. The behavior of titanium containing three interstitial elements has hitherto not been investigated in any detail, but is the topic of ongoing research in the authors' lab. For example, the mixed interstitial solubility is presently unknown. Fig. 6 shows a CP titanium grade 2, which contains all three interstitial in the surface region. The treatment was performed by firstly carbo-oxidizing the sample followed by nitriding. The hardness profiles shown in Fig. 6 are divided into two: a profile for the diffusion zone (interstitials in solid solution in metallic titanium) and one for the compound zone/network. The effect of adding nitrogen by a post nitriding treatment to a carbo-oxidized sample is obvious. There is a marginal change in hardness for the compound(s), which suggests that substitution of O and C by N does not occur to any large extent or that the substitution does not result in a change in hardness.

However, the diffusion zone is markedly affected by the addition of nitrogen; the hardness increases in the entire diffusion zone. Hardness values reaching 1800-1900 HV are obtained for metallic titanium, which indicate an augmented interstitial solubility by the presence of several types of interstitials. Evidently, the presence of mixed interstitials can result in a very high solubility in titanium. This is an unprecedented high hardness in metallic titanium; interestingly, the material does not appear brittle (the very high hardness in mind). A more “practical” way of illustrating the applicability of surface hardened titanium containing N, C and O is also shown in Fig.6: a treated and mirror polished flat plate is contacted with a mechanical tool – the surface is extremely scratch resistant even when applying “brute” force on the surface.

In addition to very high hardness and extreme wear resistance (not shown herein) is chemical resistance of mixed interstitial phases. As stated in the beginning, mixed interstitial compounds are claimed to possess different physical and chemical properties compared to the single interstitial systems. The corrosion resistance of carbo-oxidized titanium grade 2 is shown in Fig. 7. A treated and an untreated sample were submerged in a solution containing 0.25 wt.% HF with pH=1. The untreated titanium sample corroded upon contact with the solution exhibiting violent gas development and after 16 days of exposure the sample had lost 10% of its original weight; the carbo-oxidized part was unaffected after 16 days of exposure. This resistant behavior can be attributed to the chemical inertness of mixed interstitial phases. In addition to mixed interstitial compounds also so-called Magnéli phases (see [12,13]), which are sub-oxides of Ti that have a graphite like structure with the general structure Ti_nO_{2n-1} (where n= 4 to 10), can be produced together with the carbo-oxides (results not shown here). Magnéli phases also possess highly intriguing properties, e.g. special electrochemical behavior, very high corrosion resistance in certain media and photocatalytic and lubricating properties.

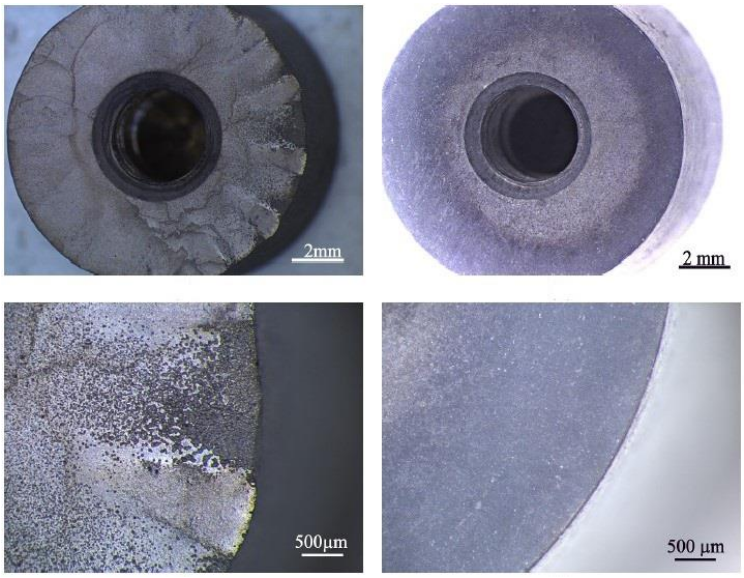

Fig.7 – Stereo microscopy of corrosion exposed titanium grade 2 after 16 days in a 0.25 wt% HF solution with pH=1 adjusted with HCL. Left) no surface treatment; Right) after carbo-oxidation. The surface treatment renders the material fully corrosion resistant, i.e. no material loss is detected; the untreated part loses approximate 10% of its weight by corrosion [11].

Future trends: surface hardening of AM parts

The advent of additive manufacturing techniques, in particular 3D metal printing, has paved the way for a renaissance in the use of titanium and titanium alloys. Titanium is one of the materials of choice for 3D metal printing. The technique can exploit the favorable properties of titanium and to some extent overcome one of its weaknesses, which is price. Printed parts have a highly beneficial “buy to fly” ratio, i.e. a term used for conventional processing on how much material needs to be machined away in order to arrive at the desired

shape. 3D parts are typically printed with internal voids and hollow structures – see an example of a 3D printed part, a so-called pulley wheel for a high-end racing-bicycle, in Fig. 8. The printed part is extremely light-weight due to the use of titanium (grade 5) and the internal hollow structure. A weak point for this specific application is the poor wear resistance of the part; a remedy for this is found in surface hardening. Also, in Fig. 8 is shown a carbo-oxidized pulley wheel (black surface finish).

Fig.8– 3D printed pulley wheels in titanium grade 5 (printed by the Danish Technological Institute, DTI). Left) Part after post finishing; Right) after surface hardening (carbo-oxidation) – cf. treatment in Fig. 9.

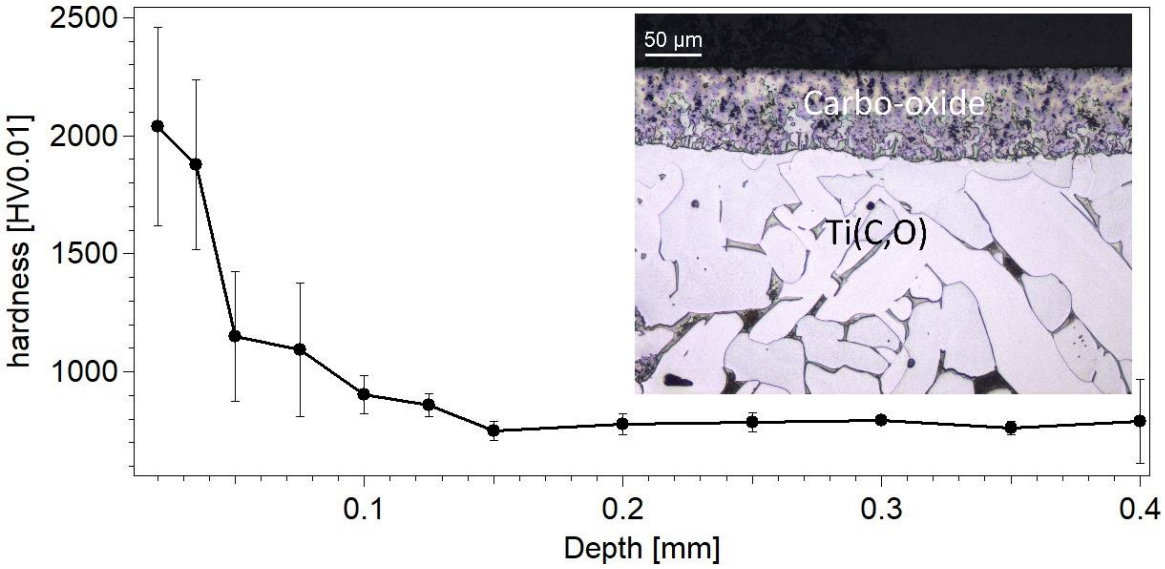

Fig.9. Carbo-oxidized 3D printed titanium grade 5. 1050°C / 16 hours in a carbon and oxygen providing atmosphere. Left) micrograph showing a dense surface layer of hard carbo-oxide and an underlying diffusion zone of oxygen (and carbon) in solid solution in titanium. Right) Hardness depth profile [14].

The microstructure of carbo-oxidized 3D printed titanium grade 5 (not the pulley wheel but a printed test cube) is shown in Fig. 9. The microstructure of carbo-oxidized titanium grade 5 is different from grade 2 due to the presence of Al and V; Al is a strong oxide former and influences the growth mode of the compound layer (cf. above). The carbo-oxidation yields an extremely deep zone, which actually penetrates through the part. The micrograph in Fig. 9 shows a well-defined and uniform surface layer of mixed interstitial compound (carbo-oxide). Below the compound layer is a diffusion zone consisting of relatively large alpha grains or alpha region stabilized by a high interstitial content (mainly oxygen). This zone extends beyond the area depicted in the micrograph. The hardness-depth profile given in Fig.9 reflects the outermost compound layer, which has a hardness of more than 2000 HV. The remainder (up to 0.4 mm depth) is the diffusion zone. Such carbo-oxidized 3D printed grade 5 components possess an excellent wear and corrosion resistance.

SUMMARY AND OUTLOOK

Surface hardening of titanium and titanium alloys has hitherto been considered somewhat niche due to limited process possibilities. The present paper has shown that new routes exist for performing chemically controlled low temperature surface hardening by using oxygen as a hardening element. Low temperature oxidizing results in deep diffusion zones where oxygen is in solid solution in the titanium and with a gradual transition from the surface to the core. Zirconium has a largely similar response as titanium on surface hardening by an oxidation treatment. Zirconium can form a hard and dense oxide at the surface with a hardness of 1200HV.

Simultaneously, introducing several interstitial elements, leading to mixed-interstitial phases, results in deep hardened cases with a very high hardness, i.e. in the range 2000 to 3000 HV. Mixed interstitial phases can be obtained in CP titanium but also in alloys of titanium, e.g. grade 5 and Ti13Nb13Zr. Introduction of nitrogen, carbon and oxygen in titanium results in unprecedentedly hard metallic titanium reaching values up to 1900 HV. The corrosion resistance in HF containing media is vastly improved for hardened titanium containing mixed interstitials as compared to untreated titanium.

Surface hardening of 3D metal printed titanium parts is indeed possible e.g. carbo-oxidation of printed grade 5 yields a surface hardness of more than 2000 HV supported by a deep diffusion zone. It is anticipated that introduction of gas-based surface hardening methods can expand the application range of titanium and titanium alloys in the future. In particular, when AM produced parts find more widespread industrial application.

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