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Diffraction based identification of an elusive FCC phase in carbo-oxidized titanium

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ABSTRACT

A face-centered cubic (FCC) phase formed during the carbo-oxidation of hexagonal close-packed (HCP) α-Titaniu m at 600 to 700 °C. The FCC crystal structure was confirmed using transmission electron diffraction, X-ray diffraction and high angle annular dark field scanning transmission electron microscopy. The α lattice parameter for the FCC resulting from the three methods was consistent with FCC sublattice of titanium atoms in δ-TiH 2-x . The FCC phase is hypothesized to form partly due to hydrogen pick-up, the stress state in the foil caused by the mismatch between body centered cubic iron-stabilized β-Titanium and HCP α-Titanium and the tensile stress present in front of the oxygen concentration profile. A transformation of α-Titanium into δ-TiH 2-x is accomplished by introducing Shockley partial dislocations on every 2nd closest paced plane, resulting in an orientation relation that has previously been observed for thermally induced FCC γ-Ti. The TiH 2-x phase was shown to decompose upon vacuum annealing at 500 °C.

1. Introduction

Titanium (Ti) and its alloys display a combination of favorable properties such as corrosion resistance, high specific strength and light weight [1]. The stable phases of pure Ti under standard pressures are hexagonal closed packed (HCP) α and body centered cubic (BCC) β, with the α to β transition occurring at approximately 882 °C [1]. A distinctive feature of Ti is its colloidal interstitial solubility in the metallic state, up to 33.3 at.% O [2]. Carbon can also be used as an interstitial element; however, its solubility is limited to only ~0.5 at. % C [3]. Both oxygen and carbon reside interstitially in the octahedrally coordinated interstices, causing an anisotropic expansion of the unit cell. A face centered cubic (FCC) Ti phase, designated as γ phase, that is not represented in the unary phase diagram of Ti, was firstly reported by Wawner et al. in 1969 [4]. The α to γ transformation was accomplished by applying deformation, leading to Shockley partial dislocations in the HCP phase, which results in a change of the stacking sequence from ABABAB to ABCABC, as described by [5,6]. The extensive literature on FCC γ was recently reviewed by Traylor et al. [7]. On the basis of the large discrepancy among reported lattice parameters for γ, orientation relationships between α and γ and the thermal stability of γ, it was concluded that two different types of FCC phase are reported in the literature. The first type is a CaF 2 type hydride (δ-TiH 2-x ) with an FCC sublattice of Ti atoms, induced by hydrogen pickup during focused ion beam (FIB) sample preparation for transmission electron microscopy (TEM), as first proposed by Banerjee et al. [8]. The second type is thermally induced FCC phase (γ-Ti), with the onset of nucleation occurring at 600 °C, as first observed by Yu et al. [9] using in-situ transmission electron microscopy (TEM), which also reported a complete transformation of γ-Ti into α at 700 °C. The disappearance of γ-Ti at 700 °C was also found in [10,11]. The phase appears to be promoted by the presence oxygen [7]. The reported lattice parameters for the γ phase, a FCC , scatter widely [7]; a FCC = 0.44 nm suggests a δ-TiH 2-x , while a FCC in the range 0.41–0.42 nm indicates γ-Ti. Oxygen ingress into γ-Ti can lead to an increase to 0.429 nm before transforming into TiO [7].

The parallel (habit) plane configuration between the Ti-sublattices of δ-TiH 2-x (FCC) and α-Ti (HCP) generally obeys (001) FCC ||{0001} HCP , which is expected for δ-TiH 2-x ||α [7,8,12–15]. The preceding metastable γ-TiH 4 (x < 0.67) adopts a face-centered tetragonal (FCT) sublattice of Ti atoms and exhibits the same non-close packed arrangement with α-Ti as δ-TiH 2-x . The δ-TiH 2-x phase disappears during annealing above 350 °C, caused by the release of hydrogen [16]. The γ-Ti phase adopts the...
conventional close-packed arrangement \( \{11T\}_{\text{FCC}} \{0002\}_{\text{HCP}} \), \(<011>_{\text{FCC}} \{<2110>_{\text{HCP}} \), since the close-packed plane for HCP is the basal plane [7]. The importance of the detection of the \( \gamma \)-Ti phase by X-ray diffraction (XRD), to negate the effect of H pick-up from FIB, was also emphasized in [7] and used in [17–19].

The present contribution originates from a study on the kinetics of carbo-oxidation of 25 \( \mu \)m thick thin-foils of unalloyed Ti Grade 2 in pure CO in the temperature range 600–1100 °C in steps of 50 °C [20]. Intriguing plate-shaped particles and dark ‘dots’ were formed on carbo-oxidizing at 600, 650 and 700 °C, but not at higher carbo-oxidation temperatures. The purpose of this article is to identify the nature of these microstructural features and the mechanisms involved in their formation. The results add to the understanding of hydride formation in Ti-alloys.

2. Materials and methods

The gaseous CO treatment at 600–750 °C was described in detail in [20].

X-ray diffraction (XRD) analysis was carried out using a Huber G670 diffractometer using a CuK(α)1 source in transmission (Guinier) mode, where the specimens were fixed at an angle of 45° with respect to the incident beam and rotated about the surface normal to reduce the possible influence of texture effects and enhance grain statistics. An image strip detector recorded scattered radiation in the 2θ range of 3–100° at 0.005° intervals after an exposure time of 16 h. The lattice parameters for the FCC phase and α-Titanium were determined using Rietveld refinement of intensity versus scattering angle (2θ) fractogram fitting was performed cf. [20].

Pieces of the carbo-oxidized foils were cold embedded in epoxy, ground and polished, using sequentially finer sandpaper down to #4000, followed by 3 and 1 \( \mu \)m diamond suspensions, and neutral 0.3 \( \mu \)m colloidal silica suspension as the final step for 2 min. Leftover silica particles were removed with cotton wool. Scanning electron microscopy performed in contact mode (probe: DNP-S10, Bruker). Images were acquired with a Jeol 3000F using standard SAD techniques cleaned at 5 kV and 46 pA. Further FIB thinning starting at 30 kV, 1 nA ending at 100 pA and finally lifted out and transferred to a TEM grid at 30 kV 7 nA, followed by electron probe micro-analysis [20], and is accordingly identified as β phase, because of the strong β-stabilizing effect of iron [1]. Pitting from the sample preparation can be ruled out as an explanation for the dark ‘dots’, because a pH neutral colloidal polishing agent was applied. The plates and dots are considered to consist of the same phase, the dots being a cross section of the plates that are inclined with

3. Results and interpretation

3.1. Transmission X-ray diffraction

X-ray diffractograms for the untreated and 600–750 °C samples are given in Fig. 1 (A-B), where the untreated Ti consists of α, β and tiny amounts of TiO2. Trace amounts of Fe present in the thin-foils have a β stabilizing effect; β phase was detectable after treatment up to 700 °C. Carbo-oxidation in the temperature range under consideration here leads to the formation of a NaCl type 6-TiC layer at the foil surfaces and an oxygen-containing α-Ti core, as described in more detail in [20]. FCC reflections of another cubic phase were detected in the specimens treated at 650 °C, and to a lesser extent after CO-treatment at 600 °C (at \( 20 = 35.5° \) ) and the untreated reference sample; these reflections are marked by # in Fig. 1. The corresponding lattice parameter, \( a_{\text{FCC}} \), is 0.4399 ± 0.0013 nm, which would suggest δ-TiH2. The lattice parameters for α-Ti for the 650 °C specimen are \( a_0 = 0.2954 ± 0.0004 \) nm and \( c_0 = 0.4708 ± 0.0005 \) nm, indicating predominant expansion in the c-direction by dissolution of oxygen [2]. Asymmetric broadening of the 002, peak, which is the most sensitive for dissolved interstitials in HCP Ti, is shown in Fig. 2 for the synthesis temperature range 600–650 °C. The observed asymmetric peak broadening is attributed to a non-uniform oxygen distribution in the α-Ti phase. It was concluded from kinetics analysis of carbo-oxidation that, for up to 700 °C, oxygen diffusion in h.c.p. Ti is the rate determining step in foil synthesis for (almost) the entire duration of the carbo-oxidizing treatment and that, consequently, non-uniform oxygen concentration distributions exist over the foil thickness [20].

To validate the claim that it was in fact δ-TiH2.6, vacuum annealing at 500 °C at a pressure below 1·10⁻⁶ mbar for 3 h of the 650 °C sample was performed (see. Supplementary information for patterns). This led to almost complete disappearance of the FCC peaks. Since hydrogen is the only element that can be retracted under these conditions, this is taken as proof that the FCC peaks originate from δ-TiH2.6. Evidently, the foils initially contain more hydrogen than the 60 ppm, as reported by the manufacturer [20], or additional hydrogen pick-up during carbo-oxidation from impurities in the CO and Ar gases applied.

3.2. Scanning electron microscopy

The BSE SEM images of the cross-sections of the untreated and 600–750 °C samples are presented in Fig. 3, where the observed contrast is a combination of Z-contrast and crystal orientation contrast [21]. The orientation contrast is most clearly observed for the dark-contrast and crystal orientation contrast [21]. The orientation contrast is most clearly observed for the α-Ti-grains close to the surface (see 600 °C). In the untreated foil, the small white regions distributed over the foil thickness are \( \beta \) phase, while the small dark regions are attributed to the FCC phase detected in Fig. 1 and marked as #. A few dark plates are observed. After CO treatment at 600 °C a very thin layer of TiC is present at the foil surfaces, a zone of α-Ti is present to a depth of 5 \( \mu \)m from the foil surfaces, 6 \( \mu \)m long black plates and small dark particles (up to 70 nm wide) are distributed in the α-Ti phase in the core and chunky white β-Ti particles have accumulated in the foil center. The dark particles and the plates appear to have preferred orientations within the α grains. The particles have different shapes, albeit predominantly triangular. At 650 °C, the white particles have coalesced to fewer and larger chunky regions in the foil center, the concentration of dark ‘dots’ subsides, while the lengths and widths of the dark plates have grown to about 20 \( \mu \)m and 650 nm, respectively. The ‘dots’ and plates subside further at 700 °C and have disappeared at 750 °C. The large white particles present in the 750 °C foil contain about 13 at. % Fe as measured with electron probe micro-analysis [20], and is accordingly identified as β phase, because of the strong β-stabilizing effect of iron [1]. Pitting from the sample preparation can be ruled out as an explanation for the dark ‘dots’, because a pH neutral colloidal polishing agent was applied. The plates and dots are considered to consist of the same phase, the dots being a cross section of the plates that are inclined with
3.3. Atomic force microscopy

An AFM scan (A) and the associated cross-sectional curve (B) for the 650 °C specimen is presented in Fig. 4. The plates lie about 6 nm below the average surface of the cross section, while the white spots are thought to be leftover SiO₂. A Fe stabilized Ti particle is visible in the center, visualizing the connection between the β and the plates.

3.4. Transmission electron microscopy and electron diffraction

The results of TEM investigation and selected area diffraction (SAD) are presented in Fig. 5 for the specimen carbo-oxidized at 650 °C. FCC indicates that the dark phase has an FCC (sub-)lattice; no indications of super reflections relative to FCC (nor HCP) were observed. The orientation relation between FCC and HCP was identified as {111}FCC//{0002}HCP, <110>_{FCC}<110>_{HCP}. The diffuse lines connecting the FCC spots to HCP, are attributed to lattice strains, originating from the slight misorientation between HCP-FCC across interface to accommodate the volume misfit. The corresponding dark field (DF) image shows that the FCC phase has a length of 1.1 μm and 100 nm, i.e. commensurate with the dark dots in Fig. 3. The misorientation angle between FCC and HCP lattices was measured as 1.7°, while the lattice parameter obtained is a_{FCC} = 0.444 ± 0.003 nm, which is consistent with the value determined from XRD (cf. Section 3.1). The lattice parameter would correspond to a volume per Ti atom, V_Ti = 21.3 nm³ and is consistent with δ-TiH₂ [22]. The dark contrast of this phase in BSE imaging in Fig. 3 would be in agreement with a lower average atomic number than the α-Ti phase.

Fig. 2. Arbitrary peak intensity and position from Fig. 1 showing asymmetric peak broadening of 002, in 600 and 650 °C specimens relative to the 700 and 750 °C. Asymmetric broadening is attributed to a non-uniform oxygen distribution over the foil thickness.

<table>
<thead>
<tr>
<th>002 Peak</th>
<th>600 °C</th>
<th>650 °C</th>
<th>700 °C</th>
<th>750 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity / Arbitrary units</td>
<td>1.111</td>
<td>0.612</td>
<td>0.112</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Fig. 1. Transmission x-ray diffractograms for the untreated and 600–750 °C samples. Identified phases: HCP, α, β-TiFe, TiO₂, Ti₅C₃, and FCC. (B) diffractogram sample identification applies to the (A) diffractogram.
0.484 ± 0.004 nm, while the $c_\alpha$ in (A) is measured as 0.494 ± 0.004 nm. A HAADF-STEM image of the interface between the HCP and FCC is shown in Fig. 7 (C), with a higher magnification in (D). As the yellow and green lines demonstrate, the lattices are misoriented by 2.3°, commensurate with the misorientation observed in Fig. 5 (B).

4. Discussion

The identification of the cubic phase mainly relies on the determined values for $a_{\text{FCC}}$. XRD (cf. Fig. 1) and SAD (cf. Fig. 5 (B)) provide consistent values indicating the presence $\delta$-TiH$_{2-x}$ [7]. A slightly higher $a_{\text{FCC}}$ value determined with SAD could be explained from additional hydrogen pick-up during FIB sample preparation, provided that the difference is significant and not within experimental accuracy. The $a_{\text{FCC}}$ determined with HAADF-STEM (Fig. 7) is about 10% larger than the values determined with XRD and SAD. Generally, among the three applied methods, HAADF-STEM is the least accurate to determine lattice spacings. Clearly, neither of the determined values would be consistent with $\gamma$-Ti, irrespective of the presence of whether $\gamma$-Ti is oxygen induced, because the most accurate of the techniques (XRD) indicates a lattice parameter well beyond those for $\gamma$-Ti. On the other hand, the orientation relationship between HCP and FCC would suggest $\gamma$-Ti. Since shear stresses are considered the primary driver for the HCP – FCC transformation in the present case (see argumentation below), it is
Fig. 4. AFM image of the dark plates in the 650 °C specimen, with a cross-section curve drawn to show the depth of the plates.

Fig. 5. (A) BF micrograph of FCC lamella and HCP matrix with indicated SAD regions. (B) SAD patterns acquired from the region in (A). (C) DF micrographs from spots indicated in (B) showing a FCC lamella with a lattice parameters of 0.444 ± 0.003 nm.
anticipated that $\{111\}$ FCC $||\{0002\}$ HCP also applied for the $\delta$-TiH$_{2-x}$ in $\alpha$-Ti.

The concentration gradient of O plays an important role in the formation of the FCC phase in the centre of the foils. For the relatively low carbo-oxidation temperatures applied here, the relatively enhanced O content in the surface adjacent part of the foils stabilizes $\alpha$-Ti and suppresses $\beta$-Ti. After treatment at 600 and 650 °C a very low oxygen content is present in the foil centre as described in [20]. The $\beta$ phase is initially distributed throughout the untreated foil (cf. Fig. 3), but is driven inwardly, ahead of the O diffusion front, due to the low solubility of Fe in $\alpha$-Ti [24], which is strongly stabilized by interstitial dissolution of oxygen. Since Fe diffuses faster in $\alpha$-Ti than O, this leads to an accumulation of Fe in the core of the foils, thereby stabilizing the $\beta$ particles in the center of the foils [20]. Also, carbon can diffuse faster than oxygen. Further, it is noted that the solubility of H in $\alpha$-Ti can be spectacularly augmented through stabilization of the HCP lattice by the dissolution of high amount of relatively large interstitials as O (and N) [22]. This could explain why $\delta$-TiH$_{2-x}$ in not observed close to the surface for the lower synthesis temperatures and has entirely disappeared at higher temperatures where the oxygen distribution is uniform and the O content higher.

Recognizing the volume expansion associated with the dissolution of O in $\alpha$-Ti and the oxygen concentration gradient, it is expected that, at the carbo-oxidation temperature, a state of tensile stress (parallel to the plane of the foil) is present in front of the O profile while the oxygen containing part experiences compression. Further, on cooling, around the $\beta$ particles a strain distribution is anticipated, as a consequence of differences in the coefficients of linear thermal expansion (CLE) of $\alpha$ and $\beta$ phase, such that the latter shrinks most [24]; higher O contents in $\alpha$-Ti appear to enlarge the mismatch in CLE between $\alpha$ and $\beta$ [25]. Combining the above stress distributions developing on synthesis and subsequent cooling, it is likely that shear stresses result in the centre of the foil in the vicinity of the $\beta$ particles. It is hypothesized that these shear stresses enable the transformation of $\alpha$-Ti into FCC (during cooling), under the rapid ingress of H into the FCC lattice and thereby explain an orientation relation with $\alpha$-Ti that is generally observed for $\gamma$-Ti, but not for $\delta$-TiH$_{2-x}$.

The rapid transformation of $\alpha$ into $\delta$-TiH$_{2-x}$ by a pseudo-martensitic transformation by Shockley partial dislocations was also proposed in [22]. It is also expected that the elusive FCC phase forms below the eutectoid temperature in the Ti–H phase diagram i.e. 300 °C [26].

Fig. 6. (A and C) SAD patterns acquired on the FCC lamella with two different tilts, with respective planes and orientations for HCP inserted. FCC spots are visible due to double diffraction, with index not being possible. (B and D) DF micrographs from spots indicated in (A and C), with bending contours being visible in (C) due to strain release during FIB in the HCP.
Tensile stresses in the center of the foil state does not emerge for a uniform O concentration profile. This circumstance, together with the enhanced H solubility in O-rich $\alpha$-Ti [22] explains why FCC is hardly observed for synthesis temperatures above 700 °C.

5. Conclusion

The characterization of the carbo-oxidized Ti foils yielded the following conclusions:

• According to literature, the $a$ lattice parameter for FCC phase observed in Ti is either 0.44 nm or 0.41–0.42 nm, with the former indicating the CaF$_2$ type hydride $\delta$-TiH$_{2-x}$ and the latter suggesting the $\gamma$-Ti phase [7]. The present study finds $a$ lattice parameters of 0.439, 0.444 and 0.484 (+/- 0.004) nm, from X-ray diffraction, transmission electron diffraction and high-angle annular dark-field scanning electron transmission electron microscopy, respectively. The high values consistently identify the formed FCC phase as $\delta$-TiH$_{2-x}$.
• The orientation relation between $\alpha$ and $\delta$-TiH$_{2-x}$ was determined as \{Ti$_1$FCC\}||\{0002\}_{HCP}, <110>$_{\text{FCC}}$$<1\text{T}0>_{\text{HCP}}$, which would suggest $\gamma$-Ti [7]. However, because the $\delta$-TiH$_{2-x}$ formation is assisted by the presence of shear stresses and the introduction of Shockley partial dislocations, it is anticipated that this close packed arrangement will form, despite the generally observed \{001\}_{FCC}||\{0001\}_{HCP} for $\delta$-TiH$_{2-x}$.
• High vacuum annealing at 500 °C removed hydrogen from the foil and with it the elusive FCC phase disappeared, which is further proof that the FCC phase was indeed $\delta$-TiH$_{2-x}$.
• The formation of the $\delta$-TiH$_{2-x}$ was made possible by hydrogen ingress into the foil during carbo-oxidation and from hydrogen initially present in the foil. The complex stress state in the center of the foil assists in the local transformation of $\alpha$-Ti into $\delta$-TiH$_{2-x}$ by introduction of Shockley partial dislocations on the densest packed planes. Hydrogen solubility in $\alpha$-Ti is augmented by lattice expansion due to dissolved oxygen; a higher O content and a more uniform O concentration distribution at higher carbo-oxidation temperature, resulted in avoidance of the $\delta$-TiH$_{2-x}$ phase.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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