

# Study of Cavitation Erosion Experiments on Thermally Oxidized Rutile Phase TiO<sub>2</sub> Films on Stainless Steel

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**Abstract** A technique to deposit titanium films with rutile-TiO<sub>2</sub> layer at the top was carried out in two steps: the deposition of titanium by means of cathodic vacuum arc (CVA) followed by a thermal oxidation technique was investigated. As a result, well adhering rutile films occurred in the near surface region. The uncoated and coated substrates were investigated using X-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDX). The presence of rutile phase titanium dioxide and titanium metal was confirmed by XRD. Cavitation erosion was used to investigate the protective adhesion properties of these coatings. Cavitation erosion tests confirmed that rutile TiO<sub>2</sub> films with a Ti inter layer adhere well to stainless steel substrates and protect the substrate from erosion.

**Keywords:** titanium dioxide, TiO<sub>2</sub>, rutile phase, cathodic vacuum arc, thermal oxidation, cavitation erosion

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) is a semiconducting material which may be used in a wide variety of technology applications such as temperature sensor, photocatalysis, electrolyte in solar cells, gas sensor, white pigment, corrosion protective coating, and optical coating, in memory devices, and as anode material Li batteries [2,3,4,5]. TiO<sub>2</sub> exists in three common modifications: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). Under ambient conditions, macrocrystalline rutile is thermodynamically stable relative to macrocrystalline anatase and brookite [1]. TiO<sub>2</sub> thin films can be deposited by several techniques, such as sputtering, chemical vapor deposition, pulsed laser deposition, and sol gel methods [3,6,7]. In order to deposit rutile phase using techniques like CVD, sol gel, etc., high temperature is necessary. But due to lattice mismatch and thermal expansion mismatch between rutile phase and the stainless steel substrate, rutile films cannot be deposited with good adhesion on stainless steel substrates [7]. However a layered film structure (TiO<sub>2</sub> or Ti) shows good adhesion on stainless steel substrates. This layered film structure can be obtained by thermal oxidation of titanium films to rutile phase [8].

Thermal oxidation is a widely used surface engineering process to improve the anti-corrosive and anti-wear properties of Ti-based coatings and alloys [9]. This process is normally carried out at high temperatures in a controlled atmosphere. The thermal oxidation treatment generates a hard oxide layer on the sample surface and an oxygen diffusion zone beneath it and improves the

material hardness and their anti-corrosive properties [10].

Krishna et al [11] reported layered films over stainless steel by magnetron sputtering. Those films show good adhesion properties with stainless steel substrates, and enhance the surface hardness and tribological properties of stainless steel. In the present work, similar layered films were developed by thermal oxidation of titanium films deposited using CVA technique. Cathodic vacuum arc has been chosen here for developing titanium films as the deposition rate is high [12]. Hence, it is promising for mass production.

So far, various techniques used to evaluate the film adhesion are given in the literature, e.g. Laser-acoustic, the bending test, the scratch test, the Rockwell test, and the cavitation erosion test [13,14,15]. Ollendorf et al [13] reported a comparative study of the above mentioned techniques to estimate the adhesion behavior of Titanium nitride (TiN) films on steel substrate. As a result, some of the cited methods unsuccessful such as the impact test or the Rockwell test.

Additionally, F. Deuerler and co-worker [16] shows that the cavitation erosion technique was successfully utilized to evaluate the adhesion behavior on other systems, e.g. diamond coatings [16] or metal films on polymer substrates [17]. Thus it seems to be promising technique for the TiO<sub>2</sub> films on steel substrate. To the best of our knowledge, testing the adhesion properties of TiO<sub>2</sub> films on steel is by cavitation erosion has not been previously reported. The research topic is of general interest. The work described in this manuscript shows an effective process of producing rutile film with improved adhesion to stainless steel substrates, and introduced the cavitation erosion method to evaluate the coating adhesion.

## 2. Experimental Section

The preparation of titanium films with rutile-TiO<sub>2</sub> layer at the top was carried out in two steps: the deposition of titanium by means of cathodic vacuum arc (CVA) followed by a thermal oxidation technique, as explained in the following.

### 2.1. Deposition of Titanium on Stainless Steel Substrate

Titanium coatings were deposited by a cathodic vacuum arc (CVA) method. The titanium with purity grade 2 (Ti (99.3%)) was used as the cathode source. Coatings were performed in the presence of argon gas (99, 99 % purity). Inside the chamber, the position of the sample holder is fixed in front of the source and the distance between these objects was maintained at around 55 cm. All coatings were deposited on unpolished stainless steel substrates ((AISI 304) sized 2cm x 3cm), which were cut out of a large metal sheet. Before deposition the substrates were cleaned in an ultrasonic bath with acetone for 10-15 minutes. For the measurement of the deposited film, the substrate was weighed before and after depositions using a high precision weight balance (Sartorius, model CP225D). From the change in the mass the thickness of the films was calculated by using the density of bulk titanium [2,18].

The following describes the typical process for titanium coating by CVA, as also used in the current work. Initially the substrate was cleaned by argon plasma at 0.75 torr and a negative bias voltage of 1000 Volt for 10 min. During the deposition of titanium, voltage and current were kept constant at 20 Volt and 80 amperes simultaneously. All deposition coatings were carried out at 0.75 torr.

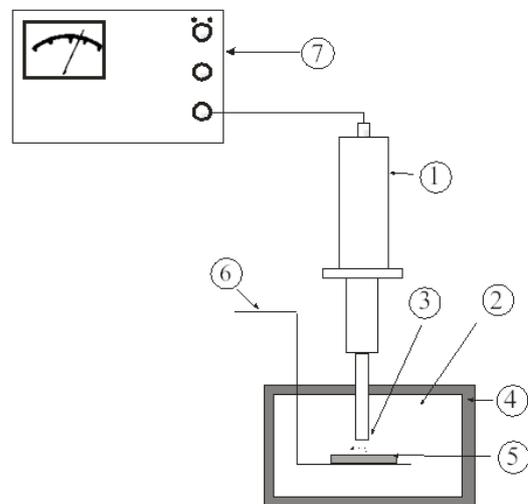
### 2.2. Thermal Oxidation of Titanium Coating

After the deposition of titanium from CVA the samples were oxidized by keeping them in a furnace in an oxygen atmosphere (oxygen flow of 200 standard cubic centimeter (scm)) at various temperatures, ranging from 400°C to 700°C for periods of 1-7 h. This temperature region comes within the sensitization temperature range of stainless steel (450°C - 850°C) at which carbon from SS304 precipitates into the grain boundaries and makes it more prone to intergranular corrosion. Normally, Ti acts as stabilizing element due to its high creep- and intergranular corrosion resistance. Annealing the Ti coated substrates at elevated temperatures as described, would help the Ti film to diffuse further into the substrates and form TiC which normally precipitates at the grain boundaries and hence, would further enhance the corrosion resistance property [19]. After oxidation treatment, the samples were removed from the furnace and allowed to cool in air. The heating and the cooling rate was 10°C/min. Mixed rutile and anatase phase appears at lower temperatures (< 600°C) [3] pure rutile phase appears only after heating at 620°C for 7h. Samples with pure rutile films were further investigated by means of cavitation erosion experiments and compared to the results of pure stainless steel. The sample are intact and the coatings well adhering.

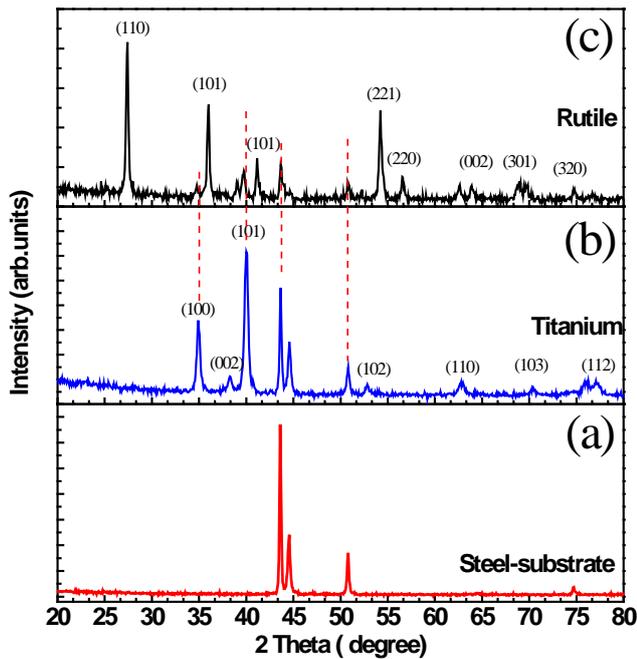
### 2.3. Cavitation Erosion Test Experiments

Cavitation erosion experiments were performed to estimate the relative adherence. A schematic diagram of the cavitation test is shown and described in Figure 1. The cavitation erosion tests of the thermally oxidized titanium films were done in accordance with ASTM G32-10 standard [14,20,21]. As illustrated in Figure 1, the main parts of the cavitation test composed of an ultrasound generator, a sonotrode with titanium tip, and a tank filled with de-ionized water which was used as the testing environment. Before the beginning of the test, the samples were cleaned and weighed. The lower end of the sonotrode was immersed 10 mm deep into a tank of the test liquid that was maintained at 20 °C and ambient pressure for all experiments. The sonotrode is vibrating at 20 kHz. Peak-to peak displacement amplitude of 50 μm was used as proposed in the ASTM standard. During the cavitation test, the high frequency vibration of the sonotrode produced a cavitation bubble field in front of the sample surface, which is caused by the pressure fluctuation at the tip of the sonotrode. Consequently, micro jets were induced by the imploding bubbles. They hit the surface, and, after a certain time, damaged it. The weight of the sample was noted after; it had been thoroughly dried, then returned to the tank for additional processing and again weighed. This cycle was repeated in order to obtain a history of mass loss versus time. To conclude, the behavior of the plot mass loss versus erosion time was used to characterize the degree of erosion.

The structures of the films were analyzed by X-ray diffraction (XRD) using a Bruker-model D8 Advance X-ray diffractometer working with Cu radiation ( $\lambda=1.5406 \text{ \AA}$ ) and grazing incidence optics. Measurements were performed for  $\theta$ - $2\theta$  configurations varying from 20° to 80°, aiming to observe the change of the structure of uncoated and coated substrates. The surface morphology was analyzed with a high-resolution scanning electron microscope (FEI ESEM Quanta 400) working with an acceleration voltage of 20kV. The SEM was equipped with energy-dispersive X-ray (EDX) analysis for the detection of the chemical composition of the films.



**Figure 1.** Schematic representation of the cavitation erosion set-up. (1) ultrasound generator 20 kHz and 25 μm, (2) de-ionized water, (3) sonotrode, (4) tank, (5) sample, (6) sample holder. (7) Power Supply (Nebatti *et al*)



**Figure 2.** XRD Patterns of (a) a clean stainless steel substrate, (b) Titanium film, and (c) rutile films which were oxidized at 620°C in O<sub>2</sub> for 7h (Nebatti *et al*)

### 3. Results and Discussion

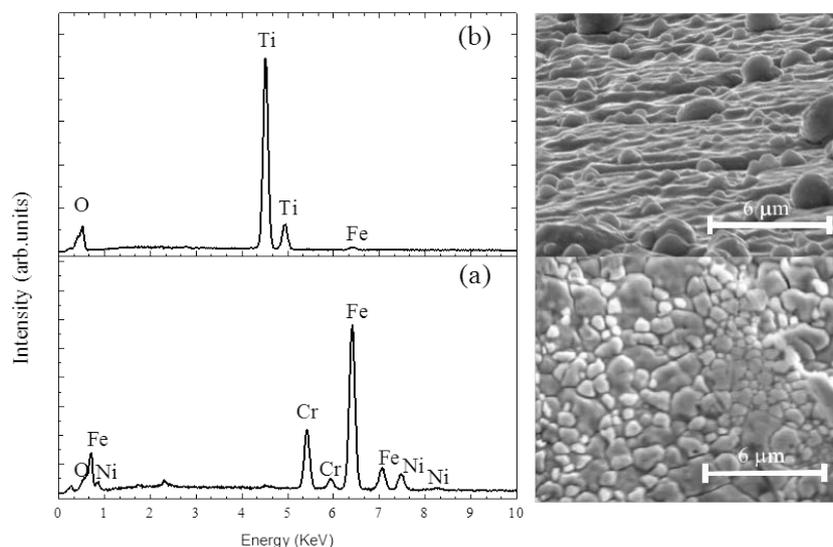
#### 3.1. Film Structure

Figure 2 shows the X-ray diffraction patterns generated from three typical samples: uncoated steel substrate (reference sample), steel substrate coated with titanium film and Ti coated steel substrate after oxidation at 620°C for 7 h. For the reference sample, four diffraction peaks can be observed, reflecting the typical structure of stainless steel [22,23]. After 20 min of titanium deposition by cathodic arc vacuum technique, film thickness of 1 μm was achieved. The XRD pattern changed: the reflection peaks of titanium were observed, which are identical to the standard pattern of bulk Ti. However, the reflections of the substrate are

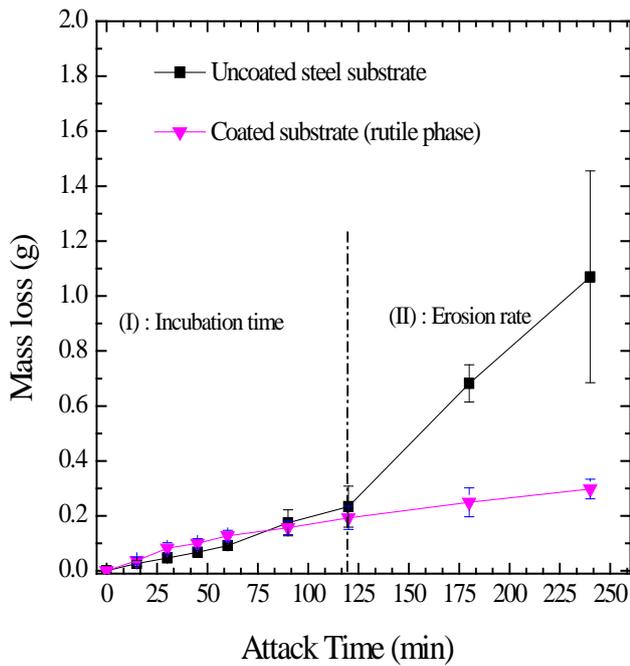
still visible. Moreover, no preferred orientation was observed in the titanium coating produced under these conditions. However, the film changed after thermal oxidation. Several titanium films were oxidized for different periods (1, 3, 5, and 7 hours) and subsequently analysed by XRD (not shown here). The appearance of peaks corresponding to the rutile phase in the diffraction pattern of 7 h oxidation suggests the formation of the rutile phase over the Ti film. XRD patterns show that rutile-TiO<sub>2</sub> also possesses a random orientation as Ti films, and becomes the major phase after oxidation. The Ti peak intensity is drastically reduced. In addition, no anatase phase was observed in the entire oxidized samples see Figure 2(c). Oxidation at these temperatures in O<sub>2</sub> environment facilitates the conversion of Ti films to rutile-TiO<sub>2</sub> [23].

#### 3.2. Chemical Composition and Surface Morphology

Figure 3 b shows the EDX- spectrum of a ~1 μm thick film, which was deposited within 20 min and oxidized at 620 °C. As a reference, the EDX-spectrum of the clean substrate is also presented in Figure 3 a. It reveals the typical spectrum of stainless steel [22,23]. The spectrum of the film in Figure 3 b clearly differs from the spectrum of the substrate: all peaks of the steel substrate could no longer be measured due to the thickness of the coated film. Furthermore, peaks of titanium and oxygen appear, indicating the formation of titanium dioxide over Ti film. In order to support the EDX analysis of both surfaces, clean substrates and oxidized titanium films were also investigated by SEM see Figure 3 (a, and b) on the right hand side. As a reference, an image of the clean unpolished substrate is shown in Figure 3a. Both images show the top view of the samples. However, before the deposition of titanium by CVA and the oxidation process, the clean stainless steel had a shining silver colored surface and small islands were observed which are separated by small trenches of 1-2 μm depth [24]. After the formation of TiO<sub>2</sub> the color of the substrate changed: green colored areas are seen and the trenches between the islands have nearly disappeared, also indicating the covering film.



**Figure 3.** SEM images and EDX spectra (a) unpolished stainless steel substrate.(b) oxidized titanium coating (after oxidation at 620 °C for 7 h under oxygen atmosphere) (Nebatti *et al*)



**Figure 4.** The variation of the mass loss versus Erosion Test Duration for uncoated steel and rutile coated steel. Each data point is the average of three cavitation test measurements (Nebatti et al)

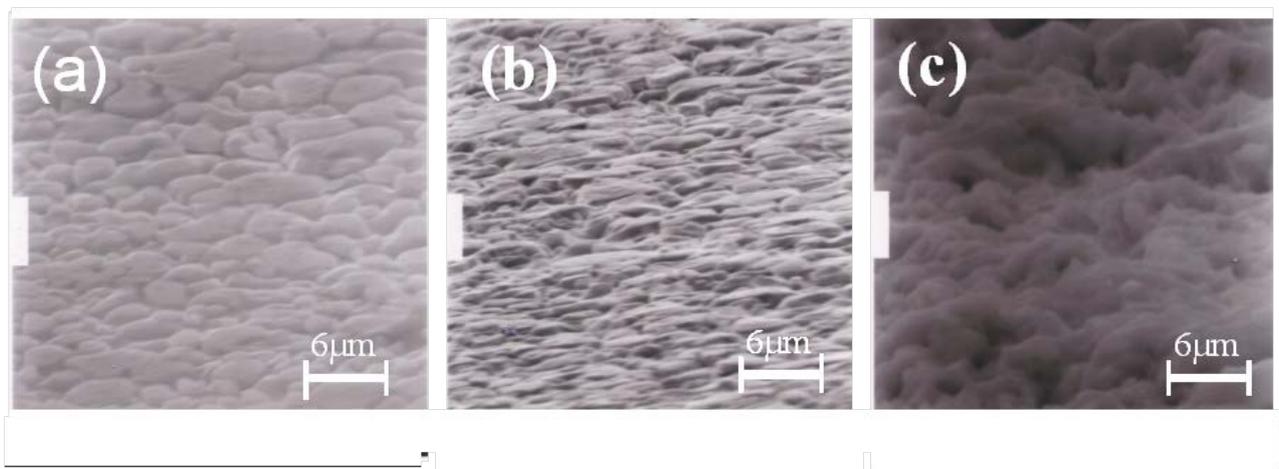
### 3.3. Cavitation Erosion Test

In order to investigate the adhesion properties of the oxidized Ti films on the steel substrate, which have an influence on cavitation resistance, the incubation time and the maximum erosion rate have been measured for both the uncoated steel and Ti coated steel with rutile-TiO<sub>2</sub> layer at the top. The tests were performed according to the ASTM-norm in order to give most comparable results [14]. Figure 4 shows the mass loss for the uncoated steel substrate and the rutile covered steel versus time. For the uncoated steel substrate, the incubation time of steel is around 120 min (area I). Further, the maximum erosion rate can be deduced from the slope of the mass loss (area II); it is around 0.637 mg/min. The endurance of the Ti

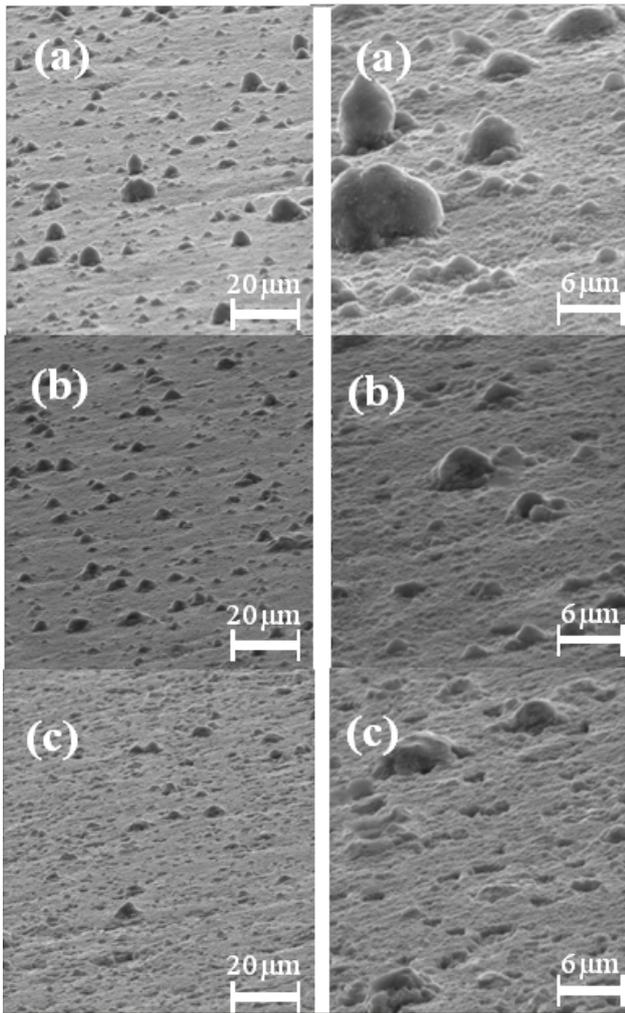
coated steel with rutile-TiO<sub>2</sub> layer at the top against the cavitation erosion differs from the uncoated steel. Within the first 60 min of cavitation, the mass loss of the coated sample is very slightly higher than that of the uncoated sample. With increasing cavitation time the mass loss of the uncoated sample rises rapidly, whereas the mass loss rate of the rutile covered samples remains relatively constant. Consequently, the difference in mass loss between the coated and uncoated steel strongly increases. The incubation time is nearly the same for the coated and the uncoated steel. For the last four points of Figure 4 the maximum erosion rate for the coated sample is calculated from the slope to be 0.932 mg/min, considerably less than for the uncoated steel. Overall, the total mass loss of the thermally oxidized samples of Ti coated steel is around 3.5 times lower than that of the uncoated sample. This is quite a promising result. Finally, it should be noted that each data point is the average of three different measurements, which were performed on three equally prepared samples and the error bars are the standard deviations.

### 3.4. SEM Analysis

The surface morphologies of the samples were also investigated by SEM in order to judge the cavitation damages visually. The uncoated steel was analyzed before the cavitation test see Figure 5(a), after 30 min Figure 5(b), and after 240 min of erosion Figure 5(c). This analysis shows that the beginning of the cavitation erosion starts slightly earlier before 30 min, which was also deduced from the mass loss calculations. After 30 min of the cavitation test, the surface of the uncoated steel shows obvious signs of the erosion process, as can be seen in Figure 5(a, b). Whilst the uncovered steel shows the typical grain structure of steel with flat islands of 10 μm diameter, before the cavitation test, several sharp edged holes of around 2 μm diameter can be seen afterwards (see Figure 5 b). As expected, the cavitation test damages become stronger after further cavitation see Figure 5(c), when the grain structure of the steel is no longer recognizable.



**Figure 5.** SEM images of an uncoated steel substrate (a-c) taken during cavitation erosion. (a) measured before the cavitation erosion test, (b) measured after 30 min, (c) measured after 240 min (Nebatti et al)



**Figure 6.** SEM images of rutile coated steel surface - (a) before the cavitation erosion test, and after (b) 30 min and (c) 240 min of cavitation erosion: left hand side images the scale bars are 20  $\mu\text{m}$ , right hand side images the scale bars are 6  $\mu\text{m}$  (Nebatti et al)

Similarly, the Ti coated steel with rutile-TiO<sub>2</sub> layer at the top was also analyzed by SEM before the erosion test Figure 6 (a), after 30 min of erosion Figure 6(b) and after 240 min of erosion Figure 6(c). In the images to the left the scale bars are 20  $\mu\text{m}$ , in the images to the right the scale bars are 6  $\mu\text{m}$ . After 30 min cavitation the surface of the coated sample Figure 6(b) is practically unchanged in comparison to its initial surface morphology Figure 6(a). Here, in contrast to the uncoated steel, no grain structure of the steel is observed to compare the surface morphology, because they are already filled with the rutile coating. After 240 min cavitation Figure 6(c) the surface morphology of the rutile covered steel is changed in comparison to the sample subjected to cavitation for 30 min and non-cavitated sample surface morphologies Figure 6(a, b). As expected, although the rutile covered steel was subjected to cavitation tests for 240 min, no grain structure from the steel was observed. This provides evidence that the coating remains. After 240 min of erosion, the uncoated steel surface is highly damaged, while for the rutile covered sample the cavitation affects only the coating. The cavitation erosion experiments presented here, have shown that the rutile film is well adhering to the steel substrate. It is further shown that the coating is improving the resistance of steel against

intensive erosion. Ti interface layer has a significant effect on the adhesion, phase formation and crystallinity of the TiO<sub>2</sub> films [25]. The Ti interface layer can relax the residual stresses caused during the formation of TiO<sub>2</sub> thereby, improving the adhesion of the rutile TiO<sub>2</sub> films onto the stainless steel substrates. Coating provides a heterogeneous nucleation condition which favors the formation of rutile TiO<sub>2</sub> films at low temperatures. Thus, Ti coated steel with rutile-TiO<sub>2</sub> layer at the top offers a good protection for the steel, which should make it interesting for industrial application.

## 4. Summary

The possibility of preparing crystalline titanium dioxide TiO<sub>2</sub> rutile phase on stainless steel substrates has been shown by the thermal oxidation of titanium. The titanium films were deposited by cathodic vacuum arc (CVA) and were thermally oxidized to grow rutile-TiO<sub>2</sub> phase at the top. With XRD and EDX analysis it was shown that the top layer of titanium films convert to rutile phase after 7 hours oxidation under O<sub>2</sub> atmosphere at 620°C. Cavitation erosion tests confirmed that rutile-TiO<sub>2</sub> with a Ti inner layer is a well adhering coating for stainless steel substrate and protects the stainless steel effectively from erosion. Hence, Ti coated steel with rutile-TiO<sub>2</sub> layer at the top should be of interest for industrial applications.

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